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XVIII.—ELECTRICAL CHARGES ARISING AT A LIQUID-GAS INTERFACE.

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Abstract.

The various methods of studying the potential differences and electric charges which arise at the liquid-gas interface are reviewed and discussed under the following headings :—

I. The determination of P.D. at the interface of liquid-gas when one or both of these is at rest.
II. Cataphoresis of gas bubbles.
III. Passage of gas over a liquid, without rupture of the latter, or of a gas over a wet solid with the same proviso.
IV. The fall of a liquid in an unbroken column through a gas.
V. Liquid jets.
VI. Waterfall electricity.
VII. Electrification produced by bubbling gases through liquids.
VIII. Electrification produced by shattering drops in an air stream.
IX. Electrification produced by spraying a liquid.

An attempt is made to co-ordinate the material obtained from this vast area of research. Many of the results may be explained in terms of the modern theory of orientation and polarisation at the liquid-gas interface, but there are other facts which do not appear to come within the scope of any established principles. Suggestions are made as to possible developments in future research.

FREE surfaces of compact matter—whether solid or liquid—are the seat of stresses which give rise to molecular adjustment, film formation, and possibly electrical separation. As such surfaces are easily accessible, they provide a promising field for the study of the constitution of matter.

There are five types of definite interface : Solid-solid, solid-liquid, solid-gas, liquid-liquid, liquid-gas. Of these, the last has received the greatest attention experimentally, being open to investigation in a variety of ways. It is the type discussed in this Paper, and we have attempted to give a summary of existing knowledge on this subject. The methods employed may be arranged under nine headings :—

I. The determination of potential difference at the interface of liquid-gas, when one or both of these is at rest.
II. Cataphoresis. The movement of a gas bubble through a liquid, by the action of an electrical field.
III. The passage of a gas over a liquid, without rupture of the latter ; or by a gas over a wet solid, with the same proviso.
IV. The fall of a liquid in an unbroken column through a gas.
V. Jets. A liquid column issuing from an orifice into a gas and breaking under the action of surface tension.
VI. Waterfall electricity. Liquid columns falling through a gas on a solid or liquid surface, after breaking up under surface tension.

VII. Bubbling. The rising of a gas bubble through a liquid with emergence at its surface.

VIII. Drop-splitting. The shattering of drops by the impact of a flowing gas.

IX. Spraying of liquid by a gas, as in the action of a scent-sprayer.

Of the above sections we notice that the first is the only statical or quasi-statical method. It has been little exploited so far, but deserves attention, for, like surface tension, it yields definite information as to surface energy. The second section is of peculiar theoretical importance. The remaining sections form a large group-subject concerned with the clash of liquid with either liquid, solid or gas, under varying conditions.

We make no attempt to describe the apparatus employed in the above methods, the processes involved being in general of a simple nature, but restrict ourselves to collating experimental results and thence deducing certain general principles.

It is impossible in a summary like this to do justice to the care and skill displayed by the many investigators who have contributed to our present knowledge. Mention will be made only of some of the more prominent, or recent, contributions to the subject. The bibliography appended in connection with each section will, however, show what authorities have been consulted.

Christiansen's term *balloelectricity* will be used to apply to electric charges, of either sign, arising from the tearing of liquid surfaces in the presence of gas.

For brevity we employ the symbols (+) and (−) in place of "positive" and "negative" respectively.

The sections classified above will now be taken in order.

I. The Potential Difference on an Interface at Rest.

Kenrick[1], using a method invented by Bichat and Blondlot, measured with an electrometer the P.D. (V_1) between the ends of a train of five materials as follows: A normal KCl solution, a liquid A, air, a liquid B, a normal KCl solution. Next he reduced the train to four members by eliminating the air, and again measured the P.D. (V_2). The difference V_1-V_2 shows the P.D. from liquid A to liquid B through air. This is clearly a differential P.D. determination of the two liquid-air interfaces.

Kenrick's results, obtained by change of materials at one of the interfaces, is as follows:—

(1) In general, a P.D. exists at a gas-liquid interface.

(2) The velocity of building the P.D. at the interface is, in general, very great. With some organic substances, however, this velocity is slow.

(3) The P.D. at the interface between solutions of highly dissociated electrolytes and air is apparently small.

(4) Certain organic substances added to a solution such as KCl in water give rise to a great decrease in P.D. at the interface. It is found that the more the lowering of surface tension the greater is the decrease in P.D. produced.

(5) The P.D. is only slightly dependent on the nature of the gas in contact with the liquid.

It is clear from these results that at a gas-liquid interface the liquid is the all-

important member in the production of P.D., and that its power in this respect is influenced by the nature of any materials it may have in solution. The explanation of the contrasting results (3) and (4) is that the organic materials mentioned are positively, and the electrolytes negatively, adsorbed.

Professor F. G. Donnan[2] quotes results by T. Thorwaldsen, who has extended this method. If a substance such as hydrochloride of methyl violet be introduced into water it reduces, or possibly reverses, the P.D. This action is attributed to the adsorption of the basic dye cation to the water-air interface.

Frumkin[3] has quite recently described a new method. At a point a few millimeters over a surface of water is placed a small burning jet, in which is inserted a platinum wire joined to an electrometer. The water is earthed through a normal electrode. Thus the P.D. water-air is found as in Kelvin's method for finding P.D. When a monomolecular layer of oil, such as olive oil, is placed on the water this P.D. decreases. The same author[4] also used Kenrick's method. He dissolved various alcohols, fatty acids, and esters in normal KCl solution, and used this as liquid A, whilst liquid B (KCl) remained constant. Varying the concentration he found the P.D. values for these organic solutes. Each family has its own P.D. extrapolated for infinite concentration (e.g., acids +0·35 volt; esters +0·61 volt). The results accord with the Gibbs's adsorption formula $q = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}$. They also indicate that orientation of adsorbed organic molecules occurs, as in the experiments of Hardy, Langmuir and Harkins, though in the latter cases the organic liquid is placed on the surface, and is not usually completely soluble.

II. Cataphoresis of a Gas Bubble.

Here measurement is made of the velocity of a small gas bubble impelled through a liquid by a constant potential difference maintained between two parallel electrodes in the liquid.

The modern researches on this subject are due to Coehn and Mozer[5], McLaughlin[6], McTaggart[7, 8, 9], and Alty[10]. We confine ourselves to the results obtained by the last two observers.

McTaggart showed that (*a*) the velocity of a bubble in water varies as the applied field; (*b*) the velocity is the same for bubbles of air, oxygen and hydrogen; (*c*) in water the movement is towards the anode; (*d*) in non-electrolytes such as pure alcohol there is no movement of the bubble. In his third Paper, quoted above, McTaggart works with bubbles in very dilute $Th(NO_3)_4$, a salt which is an active reversing agent in cataphoresis. Having freed the solution of dissolved gas, in vacuo, a bubble when introduced into the liquid dissolves and shrinks slowly enough for measurement of mobility for any desired size of bubble, from 0·62 mm. to 0·05 mm. diameter, to be made. In each experiment the bubble charge is first (−), then reduces to zero as the bubble dissolves, and later becomes (+), with reversal of motion in the field. This reversing action is proved to be due to the formation of colloidal Th $(OH)_4$ formed by hydrolysis of Th $(NO_3)_4$, and the opinion is expressed that this hydrate gathers *H* ions from the water and carries them to the surface, where they replace the OH ions normally existent there. The reversal point is in all cases attained when the bubble has dissolved to much less than its initial size.

Alty's quite recent work, while confirming much of the above, has established

further valuable results, some of which are : (*a*) The velocity of the air bubble in water is a complex function of its diameter ; the maximum velocity per unit gradient is 4×10^{-4} cm./sec./volt/cm., for a bubble of diameter 0·1 mm. (*b*) A bubble does not acquire its full charge, and so does not attain its full velocity, immediately it enters the liquid. (*c*) If the gas is soluble in the liquid, the bubble shrinks as it moves, and the rate of gas absorption greatly affects the velocity. But (*d*) if the liquid be saturated with gas there is a negative absorption, and the bubble grows for a short time after entering the liquid. (*e*) In very pure water (i.e., of conductivity less than $2{\cdot}5\times10^{-6}$ ohms^{-1}) the bubbles scarcely move, whereas in water of conductivity $8{\cdot}5\times10^{-6}$ ohms^{-1} the velocity attains a maximum. (*f*) Applying his own data for velocity to Stokes's well-known viscosity formula, Alty calculates the number of ions per sq. cm. of bubble when this attains to maximum speed.

Alty's first result, as above, is that the velocity of the bubble is a function of the diameter, whereas, as he points out, previous theory indicates that velocity would be independent of diameter. The well-known expression deduced by the Helmholtz-Lamb theory is

$$v=\frac{V\,.\,K\,.\,X}{4\pi n}$$

in which the velocity v is independent of the diameter. That the theory due to the latter writers needs modification has been pointed out for several years by Porter[11], Freundlich[12], Mukherjee[13], McBain[14], and others. The above experimental results add further evidence on this point. The double electric layer, according to the modern view, does not consist of two closely fitting skins, (—) and (+) round the bubble, but of a skin next the bubble, say (—), and a diffused cloud, say (+), outside it. Most of the (—) ions in the inner skin are " covered " by (+) ions, but there is at any instant a residuum of (—) not covered, which constitutes the (—) charge to which the bubble owes its motion in the field. Alty interprets the third of his results thus : When gas molecules are absorbed into the liquid from the bubble they move through the (—) skin, and, entering the (+) zone, upset the equilibrium there, displacing (+) ions, and so the net (—) charge increases and its velocity rises.

Some of the results of McTaggart and Alty are deducible from the Helmholtz-Lamb theory modified in respect to the composition and extent of the double electric layer. Others, such as Alty's second and third points, are explained by Alty in terms of modern views of ionic adsorption and of film formation ; but one outstanding result still calls for explanation—viz., the complex relation of velocity of bubble to its diameter.

As we shall have occasion later to refer to the interfacial P.D., it may be well to point out here that there are two kinds of potential difference. Freundlich has shown that the P.D. acting in cataphoresis is not so deep seated and not so great as that measured in Section I for surfaces at rest. The former he terms the electrokinetic, and the latter the thermodynamic, P.D.

In cataphoresis we have a phenomenon easy to study, since the controlling agent is an electric field which is readily adjusted and measured. In balloelectricity (Sections IV to IX), on the other hand, as we shall see, we are confronted with complex dynamical conditions arising in the change of shape or area of liquid surfaces. It is hardly surprising, therefore, that the theory of balloelectricity is far less advanced than that of cataphoresis. We will attempt to construct a model

of the air-liquid interface, looking to cataphoresis for much of our definite information. Imagine a liquid-air surface to be suddenly formed by the introduction of a gas bubble into a liquid composed of bipolar molecules and possibly of polymeric groups of these. We suppose changes occur somewhat in the following order :—

(*a*) Freed electrons, if any, caught on the " raw " liquid surface thus suddenly produced, tend to move into the body of the liquid, owing to their mutual repulsion.

(*b*) The surface monomolecular layer of liquid now becomes oriented. In water, at least, the inner layer (that next the bubble) is (—), the outer is (+), and Alty, in the paper quoted, gives evidence that the outer layers exert a repelling influence on the free (+) ions in the body of the liquid until its charge is neutralised by the adsorption of (—) ions. See also the work of Hardy[16], Langmuir[17] and Adam[18] on orientation. With regard to this postulated orientation, Edser[15] goes further, and suggests that the whole liquid, and not the surface layer only, becomes oriented in time. The surface orientation is a quick process and is followed by

(*c*) A slower adsorption of gas molecules from the bubble to the exposed inner side of the oriented layer. This adsorbed gas forms a layer several molecules thick inside the liquid, the strength of attachment of the several layers decreasing with distance from the liquid surface. This conception of an adsorbed gas layer many molecules thick is based on the work of many recent investigations, for instance, Evans and George[19] and Manley[20] on the solid-gas interface, and Iredale[21] on the liquid/gas interface. A gas film is not as firmly attached to a liquid as to a solid surface ; for, among other disturbances it is subjected to bombardment by liquid molecules as they emerge from, and return to, the liquid surface. As Edser points out (loc. cit.) a liquid surface is, in general, much disturbed in this way. Molecules from the adsorbed gas film will be absorbed into the liquid, others taking their place from the gas in the bubble ; this process continuing (rapidly if the gas be very soluble) until all the gas in the bubble has gone into solution.

If the liquid be a non-electrolyte, free ions do not exist, and the process about to be described, which is a necessary precedent of cataphoresis, does not take place.

(*d*) If, however, the liquid contain electrolytes, (—) ions move through it to the interface and are adsorbed there by what some writers term " chemical " adsorption. The first effect of this adsorption of (—) ions is, as we have already mentioned, to neutralise the resultant (+) field of the oriented layer. When this neutralisation has been attained, the net (—) charge on the bubble (and consequently the speed of the bubble) reaches a maximum. But as further (—) ions are adsorbed they create a field which brings up (+) ions, and the double electric layer formed by these (—) and (+) ions grows until it is complete. This layer attains a state of *dynamical* equilibrium, since both its (—) and (+) components incessantly lose and gain ions by diffusion, by heat motions of liquid molecules, and by the passage from the bubble of dissolved gas molecules.

When, as in cataphoresis, an electric field is applied to the bubble the (—) skin of the double electric layer is impelled up stream, but being strongly attached to (1)

its covering (+) ions on one side and to (2) the oriented layer on the other, it carries with it these and (3) the adsorbed gas films as well as (4) the gas bubble itself, in its migration to the anode. Of the (+) cloud of ions, the small residuum which does not act as cover to the (−) skin, moves down stream to the cathode.

If the liquid in use be water of conductivity of the order 5×10^{-6} ohms^{-1}, the water ions are OH (−) and H (+). When to this water is added a salt, the ions of the salt are adsorbed to the interface, bringing about changes in the films and affecting the mobility of the bubble. In the case of some salts the mobility is merely reduced; where, as in the case of those possessing multivalent cations, such as $Th(NO_3)_4$ and $La(NO_3)_3$, the mobility is reversed, showing that the net charge on the inner skin of the bubble is(+), the original (−)OH ions having been replaced in part at least by the (+) cations.

III. Passage of Gas Over Liquid.

A succession of writers, Allessandri[22], Wolf[23], Bloch[24], Rey[25] and J. J. Nolan and Gill[26], have all demonstrated that no balloelectricity arises by the mere rush of gas over a liquid surface, even though the latter be raised into ripples.

Again, Kelvin, Maclean and Galt[27] in 1895, and Himstedt[28] in 1902, showed that air passed over wet pumice or coke acquires increased conductivity; but as in neither investigation is it made clear that the ionization thus found in the air is not in reality due to the breaking of the liquid attached to the solid surface in a species of bubbling, we must exclude the results for the purposes of this section.

Several investigations have been made in connexion with evaporation and boiling. Faraday[29] established that simple evaporation of water, as also condensation of water vapour, is unproductive of charge. Again, Blake[30], Schwalbe[31], Beggerow[32], Gallarotti[33], and Henderson[34] have shown that evaporation of water, charged or uncharged, does not give rise to charges. Evaporation and condensation are processes which involve the passage through a surface of *single* molecules. Even in the violent process of the boiling of water the emerging vapour appears to heal any ruptures in the surface which it may produce in breaking through, and so precludes any escape of electrons or ions. So, as in none of these cases is the liquid surface torn into a "raw" condition, no balloelectric charges arise. Holmgren[35] claimed to have found (+) charge in water and (−) on the air when the latter produced ripples on the surface; but J. J. Nolan[26] and Rey[25] have recently disputed this result.

IV. Fall of a Liquid Column Through a Gas.

Both Lenard[40] and Aganin[36] have shown that if a jet of liquid meet a liquid surface *before breaking up* under the action of surface tension, no charge is developed in it or in the gas through which it passes. We note that the criterion for charging is the rupture of a liquid surface.

We learn from this and the preceding section that mere *friction* between gas and liquid does not, *per se*, cause electrical separation. Later we shall see that any process of rapid *rupture* of a liquid surface does, in general, generate charges.

V. Jets.

Lord Rayleigh[37] published a series of researches on the conditions, dynamical and electrical, in a jet of liquid rising nearly vertically from an orifice. The column

of liquid breaks under surface tension into a swarm of droplets varying greatly in size and speed. Consider three cases : (1) Just after the breaking point of the column there is a region in which the droplets collide and rebound, and we have the familiar scattering of the drops. (2) When a small electric charge is brought near the jet, a potential difference is established within the jet. Rayleigh showed that if this potential difference lies between certain limits the drops acquire differential electrification, and in consequence are attracted to one another so strongly that if they collide in the jet their skins break and coalescence occurs. (3) If, however, a greater potential difference be established by bringing the electric charge nearer, the large mutual repulsion of the similarly charged drops prevents collision, and scattering once more occurs. Thus we have scattering due in the first case to collision and rebound, in the second to electric repulsion.

In connexion with the phenomenon of collision (1 above), Rayleigh showed that there exists a large electrical insulation between two clean water jets if they meet before breaking up. We have already noted that a water surface has a monomolecular oriented layer, and possibly the beginning of an adsorbed gas layer, provided a small fraction of a second has elapsed since the time of formation of that surface. These films are in composition unlike the body of the liquid, and we suggest may provide both the strength necessary to resist coalescence and this high insulation which is not broken down even by the considerable shock of collision. Hiss[38] showed that 0·008 sec. after the formation of a water surface the surface tension has fallen 9 per cent. from its first value. This result indicates that film formation is a rapid process.

Another observation made by Rayleigh was that a small amount of dust or grease on the jets, by upsetting the continuity of the surfaces or by lowering the surface tension, conduces to coalescence. Again, certain gases, especially soluble ones—e.g., carbon-dioxide and sulphur dioxide—surrounding the jet have a like effect.

Burton and Wiegand[39] in experiments on jets, applied known electrical fields near the orifice, and found (1) that the size of the drops is not affected by the field ; (2) that however large the applied field there is an absolute alignment of the drops for at least a part of their journey ; (3) for small fields coalescence occurs in the region of low velocity—i.e., at the summit of the trajectory. These authors suggest a theoretical treatment of the problem differing from that of Rayleigh. To account for the action of droplets on one another, they employ Kelvin's solution of the problem of the interaction of spheres charged alike.

Aganin[36] employed very small orifices to produce jets. He observed the jets with a microscope at a point just beyond the breaking point, and found that at this point the speed differences of the droplets are so great that collision is frequently followed by coalescence. Further along the jet, speed differences are reduced by viscosity of the air, and hence, as already observed by Rayleigh, coalescence no longer results from collision.

Two other points were established by Aganin.

(1) No charge ever arises at the orifice itself.

(2) In the earlier history of the broken jet, when coalescence of drops occurs, the air surrounding the jet receives a charge.

We shall see in later sections that the *rapid* tearing of a matured water surface generates charges. So, in the breaking up of a jet by surface tension we might

expect like effects, the surface in this case also being torn after maturing. But, among balloelectric processes, jets are peculiar in that, in their case, the breaking of the surface is spontaneous. Except in the last stages of the pinching off of the drops, the formation of new water surface is a relatively slow process. In the limit, when the drop is actually pinched off at the breaking point of the jet, relatively few molecules remain in the cross section of the "neck" between it and the column; and the actual tearing process is confined to these few. As each pair of molecules torn asunder would liberate only one or two ions, the total charge arising would be small. Lenard[54] in his Paper on the general theory, allows that *small* charges may arise in this way; while J. J. Nolan and Enright (60, p. 3) state definitely that a small charge does arise.

Kelvin, Maclean and Galt[27] surrounded a column of water falling from a tap by a long tube joined to an electrometer, and observed charges in the air. But if, as seems possible, any falling drops struck the tube, and so generated waterfall electricity, their result must be omitted for the purposes of this section.

VI. Waterfall Electricity.

This is Lenards name for a subject of which he is the pioneer. Here we deal with the conditions arising when columns of liquid in passing through a gas break under surface tension into drops and then strike solid or liquid surfaces. Lenard and Aganin have shown that no charges arise unless the column breaks before striking occurs.

The influence of the gas through which the liquid (water) passes was investigated by Lenard[40] and by Sir J. J. Thomson[41] with proportional charges as below :—

	Thomson.	Lenard.
Air	+1·0 ...	+1·0
Coalgas ...	+0·41 ...	+0·86
Hydrogen ...	−0·11 ...	+0·65

These figures show the relative charges developed in the water after impact. The results differ greatly in amount, and in one case in sign, and we have an instance of the great influence exerted in this class of experiment by small—scarcely detectable—differences in the composition of the water or of the gases used.

Lenard allowed various liquids to descend through air, the results for the charges found in the liquid being, e.g., water (+1·0), ether (+0·01), mercury (+14·3).

In the above experiments the charges in the *liquid* are measured. Other investigators, Becker[42], Aselmann[43], Kähler[44] have measured the charges in the air over the liquid. For pure water Aselmann and Kähler found only (−) ions; but for solutions of common salt, both (+) and (−) ions in the air. Becker experimented with mercury falling through various gases (air, carbon dioxide, hydrogen) on to the surface of various metals. The resulting ions in the air are in some cases (+), in others (−), the numerical values also differing very greatly according to the metal employed. He concluded that each metal has its own peculiar double electric layer in air, and that the resulting charges are brought about by the joint action of the double electric layers of the mercury and of the metal struck. Becker drew up a balloelectric series, analogous to the electrochemical series, as follows :—

$$+\mathrm{Zn,\ Al,\ H_2,\ Hg,\ Air,\ CO_2,\ Fe,\ Cu,\ Pt}-$$

The interpretation of this series is as follows :—

If mercury fall on mercury in hydrogen, the gas becomes (+), but in air or carbon dioxide (—). If, however, mercury falls through carbon dioxide and descends on iron the gas is (—) ; if on aluminium (+).

Lenard[40], J. J. Thomson[41] and Rey[25] have shown that an electrolyte such as sodium chloride, when in small concentration in water, reduces the (—) charge in the air, and when more concentrated reverses the charge to (+). Rey has also shown that raising the temperature of the solution in such cases gives rise to increased air charge, unless the concentration of the salt is at the critical point required to give a balloelectrically neutral solution.

VIII. Bubbling.

In experiments under this heading, gas bubbles rise through a liquid until they break at its surface ; and measurements are made of the charges arising either in the liquid or in the gas above.

In the case of water this process gives rise to (+) charge in the liquid, (—) charge in the gas. De Broglie[45] divides liquids into (*a*) *active*, such as water, alcohol, ether, sulphuric acid, which give rise to charges in the air bubbled through them ; (*b*) *inactive*, such as benzene, toluene, chloroform, which give no such balloelectricity by bubbling. There does not appear to be any chemical or physical basis for this classification into active and inactive, and researches later than the above have raised doubts as to whether any such sharp division of liquids into two classes is valid ; whether, after all, the balloelectric difference between liquids is not one of kind but only of degree and sign.

Bloch[46] announced the interesting result that when an active liquid covers an inactive one, or vice versa, no charges arise on bubbling. This point ought to be investigated further, as it should throw light on the difficult problem of the nature of balloelectric activity.

Kelvin, Maclean and Galt[27] found that results depend on the nature of the bubbling gas. Thus, carbon dioxide, air, hydrogen and coal gas gave respectively, per minute, 8, 4, 2, 1·4 volts potential to the water through which they bubbled. Let us contrast this with McTaggart's results (Section II) that the nature of the gas has no effect on cataphoresis of a bubble—i.e., does not influence the double electric layer. It follows that we cannot regard the double electric layer as the seat of most of the charges found by Kelvin, Maclean and Galt. But we have seen that the moving bubble carries with it (*a*) an adsorbed gas layer and (*b*) a water layer more or less saturated with dissolved gas. To one or both of these two layers we may look for most of the balloelectric charges varying so greatly in the results just quoted.

Fischer[47] showed that water vapour rising through water generates no balloelectricity, a fact which, combined with those just quoted, proves that for the production of charges the gas and liquid phases must be chemically different. Another significant result due to Fischer is that small bubbles give greater charges than large ones for the same total volume of gas passed. This result might have been anticipated ; the pressure in a bubble is $2T/r$, so small bubbles will explode on reaching the surface with violence proportional to their curvature ; and we shall see in Section VIII that violence and rapidity of surface explosion conduce to large charges.

Coehn and Mozer[48] investigated the effect on the charges in the gas (pure oxygen or hydrogen) when various salts, acids, alkalis, etc., are dissolved in the water used. Using only *very pure* liquids, they found that non-electrolytes and solutions of these in water gave only (−) ions in the gas. On adding electrolytes (+) ions appear, and as the concentration of electrolyte increases these (+) ions increase in number, till the (−) and (+) occur in equal number, and further concentration leads to a surplus of (+) with reversal of net charge. The effect on the water will thus be that as the concentration of the electrolyte increases its charge will be reduced from (+) to zero and then reversed.

P. J. Nolan[49] finds, in opposition to the principle stated by Coehn and Mozer, that both (+) and (−) ions are produced in the air bubbled through alcohol, and that they are exactly equal in number.

Another result due to Coehn and Mozer is that the charge produced in a pure liquid by bubbling increases roughly in proportion to the dielectric constant of the liquid employed, using the same gas.

Coehn and Duhme[50] have quite recently investigated the bubbling of gases through various liquid metals. In the important case of pure mercury the net charge escaping into the gas is (+), but if traces of certain metals be added the sign of the charge is (−). In the case of gas bubbled through water the gas, as we know, receives a (−) charge.

Lenard, from a consideration of Becker's work, considers that the ions in the air which has bubbled through mercury are small mercury droplets. But McClelland and P. J. Nolan[51] find that they are water droplets, and can be eliminated when the materials used are well dried.

Extensive research by McClelland and P. J. Nolan[51] and by J. J. Nolan[52] on the bubbling of air through mercury and alcohol reveals the existence in the gas over the liquid in both cases of groups of ions of definite mobilities. According to this remarkable result, there appears to be a unit stable charged water globule, either (+) or (−). This unit would have maximum mobility (+) or (−). But if two (+) units coalesce with one (−) unit, there results a globule of the unit (+) charge, but of three times the mass, and hence of mobility one-third that of the unit globule. By coalescence in more complex ways, there arise globules of one-fifth one-seventh, etc., mobilities. This result—not yet explained—should throw light on the important question of the mechanism of the explosion. Nolan and Gill[2e] find that here, as in Drop-splitting (Section VIII), the charge developed is proportional to the area of new liquid surface created, but for a certain size of globule there are places of check in the curve for charge / area.

As to the nature of the explosion of the bubble, we note that since balloelectricity is manifested by non-electrolytes, we must regard the double electric layer, which is not existent in this case (*see* McTaggart's result, Section II) as not essential for the production of balloelectric charges. As the bubble approaches the surface of the liquid the skin of the latter, and the skin of the bubble, retain their (1) oriented layers, (2) adsorbed gas layers, and (3) double electric layers, so that in the limit there are six layers in all, the rest of the liquid molecules being squeezed out by the rise of the bubble. These various layers break as the gas in the bubble pushes its way through the surface and the charges subsequently found in the gas, whilst undoubtedly springing in part from the double electric layer, when it exists, are also derived from the gas layers and/or the oriented layers. The conclusion derived

from Coehn and Mozer's experiments on very pure materials and from the other principles quoted above may be put in the following form :—

Consider a non-electrolytic liquid. Both (+) and (—) components of the molecules hold together tenaceously and refuse to carry a current ; yet in the mechanical process of bubbling, electrons are liberated from the molecules and escape into the gas above ; the molecules, now charged (+), being held firmly in the liquid. On introducing an electrolyte into the liquid, a gas after being bubbled through is found to have acquired (+) as well as (—) ions, the former being derived no doubt from the electrolyte cations. Thus of the four constituents which we have considered, the (+) components of the non-electrolyte molecule is the one which most firmly resists the disintegrating force of the bubble. Reversal of the gas charge to (+) occurs at a concentration depending on the type of salt used. This reversal implies that in concentrated solutions (+) charges escape more easily than the anions and electrons jointly. This direct result is of cardinal importance, and requires interpretation.

VIII. Drop-Splitting.

Two cases, very similar, arise in this section :—

A. The impact on falling drops of a vertically rising current of gas.
B. The impact on falling drops of a horizontally moving current of gas.

The first case has been employed by many experimenters.

A.

Simpson[53], in 1909 and later, established that, for water drops of a certain average size, an uprush of air causes the drops to shatter. No shattering of such drops occurs unless the air speed exceeds 8 metres/sec., but if it does occur the droplets acquire (+) charges and the surrounding air (—) charges. The charge found on the water droplets is about 5×10^{-12} coulombs/c.c.

These results were directly opposed to Lenard's view, expressed in 1892[40], that mere dispersion of water is ineffective in producing charge. But later in 1915[54], in his comprehensive review of the subject, Lenard has modified his theory, and considers that while a *steady* air stream of 8 metres/sec. will not cause splitting and electrification, it will do so if it be sufficiently *turbulent* to give large tangentially-directed forces on the surfaces of the water drops.

Hochswender[55] repeated Simpson's experiments, and in the main confirmed his results. He published photographs of bursting drops, which show that the uprushing air first flattens a drop, then blows it into an inverted cup, and finally blows out the top of the cup and generates the charges in the air and on the droplets.

It will thus be seen that the mechanism of drop-splitting must, in its last stages, closely resemble the bursting of a bubble at the surface of a liquid ; the last stage as in bubbling, being the rending of the films peculiar to the interface.

B.

Experiments were made by J. J. Nolan[56], in which the falling drops encounter not an uprising, but a horizontal, air blast. Doubtless the effect is similar to that produced in the experiments of Simpson and Hochswender, though the relative speed of drops and air, other things being equal, is less ; and though the resulting move-

ment is not vertical but inclined. The drops would in that case be distorted and hollowed out, as in Hochswender's photographs, though in the present case the cup would be turned sideways—not inverted.

Nolan found in the emergent stream of air both (+) and (−) ions, the negative being in excess.

One significant result arising from J. J. Nolan's work is that the total charge on the droplets varies as the new area of liquid formed. Though in later work he expresses doubt as to the exact truth of this law, it appears from his results that, at least for rapid air blasts, this quantitative law is valid. Possibly Nolan's result can be interpreted thus :—

When a new surface is very rapidly formed, some of the electrons left on the "raw" surface are able to escape and charge the air (−). In that case charge varies as new area. When, however, new area is slowly formed, electrons cannot escape, and no charge arises. For intermediate speeds of surface formation, the charge cannot be strictly proportional to new area formed.

IX. Spraying.

Research in this Section has been particularly extensive. Faraday[29], working with an Armstrong electrostatic machine, proved that *dry* steam rushing along narrow passages does not produce electrification, but that it is essential for production of charges to have *water droplets* included in the blast. Doubtless these droplets have a rough journey in the narrow passages ; so that both the turbulent steam and the walls of the passages through which they pass will contribute to their decimation. The principle thus established should be borne in mind in the experiments with apparatus like ordinary scent sprayers, with which we now have to deal, since we cannot look to the rush of mere dry gas through the tube to account for any of the charges produced.

Christiansen's[57] method of procedure was unlike that of other investigators on spraying, who have generally carefully avoided splashing. His method combines spraying and waterfall processes ; the liquid was sprayed, and the resulting droplets then met a platinum plate. Investigation on the charges arising in the liquid led to the following classification of the various liquids used :—

I. *Aballisch* : Solutions of salts, acids and bases give feeble charges.
II. *Kataballisch* : Water, and its mixtures with oils, give large (+) charges.
III. *Anaballisch* : Solutions of quinine, aniline, etc., give large (−) charges.
IV. *Hyperballisch* : Mixtures of liquids from classes I, II, III give greater charge than the components used (e.g., KCl and alcohols).

Traube[58] found that those materials, such as fatty acids, alcohols and ethers, which when in solution greatly lower the surface tension of water, are kataballisch or anaballisch, whereas aballisch materials have small influence on the surface tension.

Eve[59] found that tap water, distilled water and ether all give an excess of (−) over (+) ions, the ratio of the two kinds for distilled water being 1·2/1·0. Eve obtained equal numbers of (+) and (−) ions when spraying alcohols (benzyl-, amyl- and ethyl-), acetic acid, and chloroform ; but the actual number found is much greater (two to four times) than for pure water ; in short, these materials are more balloactive. If the distilled water in these experiments were pure and contained no electrolytes it should give only (−), according to Coehn and Mozer (Section VII),

but one must remember that spraying is a much more violent process than bubbling, and this may account for the contrasting results of the two processes.

Again, in Simpson's experiments on drop-splitting of water (Section VIII), the ratio of (—) to (+) ions is 3/1 ; this ratio, higher than in Eve's results, corresponding to the less violent method of breaking the water surface.

J. J. Nolan and Enright[60], using water of varying purity, found charges increasing with the purity of the water and with its degree of pulverisation. J. J. Nolan and Gill[61] found that, although inorganic salts diminish the positive charge obtained when distilled water is sprayed, *they do not reverse it.* This is an interesting observation, as it is in sharp contrast with well accepted results of Coehn and Mozer in bubbling experiments (Section VII) and of Lenard, J. J. Thomson, Aselmann, Kähler and Rey, all employing waterfall methods (Section VI). The well attested fact is that, in these waterfall experiments, as more and more salt is added to the water the originally (+) charge on the liquid and (—) charge in the air is gradually reduced, and after a critical concentration, reversal of charge to (—) in water and (+) in air occurs. Nolan and Gill[61] to test this disparity between the spraying and waterfall results, worked the sprayer at much lower pressures than usual, but still found no reversal of sign. But with very strong solutions and extreme pulverisation the reversal appeared. But this result is by no means identical with the waterfall reversal, because in waterfall experiments the critical concentration was very weak (say 0·1 per cent.). There is no doubt about the reality of the reversal in the waterfall method ; and Simpson and Hochswender successfully employed salt to obtain neutral solutions in their work on the theory of thunder-storms.

Nolan and Gill attribute the disparity between results by the two methods to the different speed of the formation and rupture of the water surfaces. In a falling column of water time is allowed for any impurity existing in the water (perhaps an impurity occuring in the salt used) to be adsorbed to the surface, and produce its own balloelectric effect when rupture occurs ; whereas in the process of spraying an absolutely new surface is formed, and then torn so quickly that the process of adsorption is precluded. It appears that we must regard the *mechanism* of rupture of the liquid as of the same importance as the nature of the *materials* used.

Nolan and Gill investigated the reversal of charge produced when certain organic materials are dissolved in water. These materials are sodium glycocholate, sodium oleate, methylene blue, and methyl orange. A very minute amount of any of these suffices to bring about reversal, as had previously been demonstrated by J. J. Thomson[41] for methyl violet.

Nolan and Gill[61] showed that when sodium oleate is present in the water used, its balloelectric effect diminishes as the time of its exposure increases. Solutions three days old show no reversal of charge, however finely they are pulverised. Rayleigh[62] had previously shown that sodium oleate does not change the dynamical surface tension of a water jet if the surface be not more than 1/100th of a second old, the surface not having had time to mature by adsorbing the solute. De Noüy[63] has recently shown that the adsorption of sodium oleate of the concentrations used by Nolan and Gill is a relatively slow process ; thus one millionth part of sodium oleate does not affect the initial surface tension of water, but causes a reduction of surface tension 20 dynes/cm. in two hours.

Spraying is a process involving great dynamic complications. Here the top of a column of water is torn off to an unknown depth and in an oscillating manner

by rushing gas. As Nolan and Gill found, difficulties arise at the nozzle, which if not specially and accurately met, give rise to errors. These are (*a*) charging of drops by the " water-dropping " effect of Kelvin ; (*b*) electrification by friction of the liquid at the nozzle. Again, results obtained may depend on the construction and material of the sprayer used.

It is no wonder, then, that of all branches of our subject, spraying is the one in which co-ordination of results presents the greatest difficulties.

General Theories.

This summary of the subject would be incomplete without some mention of the theories propounded by Lenard and by Sir J. J. Thomson on Surface Conditions.

In 1892 Lenard published his Contact Theory, but this was replaced in 1915 by a new theory[54]. In this he postulated a complex of units in a liquid. In aqueous solutions there may exist together with the ultimate H_2O molecules, (1) polymers H_4O_2, H_6O_3, etc. ; (2) complex groups having some molecules acting as solvent, others as solute ; (3) ions consisting of a single charge with a family of H_2O molecules attached to it. These complex molecules tend to leave the surface, the forces urging them towards the body of the liquid being deduced from reasoning somewhat like that employed by Laplace in his well-known treatment of surface tension and intrinsic pressure. Further, these forces which urge the molecules as a whole, act on the massive portion of the molecules left at the surface, swinging them inwards, and so producing orientation of the surface mono-molecular layer. Lenard states that at the surface of water and all dielectric liquids there exists an electrical double layer which owes its existence to the molecular forces of the liquid. The outer layer—always negative—is identical with the outer molecular layer of the liquid. The essential of all balloelectric action is—according to Lenard—the separation of minute liquid particles from the outer layer.

About the time of publication of these views, Hardy[16], Langmuir[17] and Harkins[64] were developing, from other lines of reasoning, the modern ideas on polarity of molecules, and the consequent orientation of free surfaces.

Lenard's theory proved satisfactory in explaining balloelectric effects for pure dielectrics, and is in accord with the well-known Gibbs-Thomson adsorption relation. But his theory fails to account for

(1) The influence of the gas used in contact with the liquid.

(2) The increase in balloelectric charges due to rise in temperature of the liquid, discovered by J. J. Thomson[41] and confirmed by Rey[25].

J. J. Thomson[65] in 1914 advanced his theory of intra-molecular ionization. In certain substances termed " polar " the molecules are composed of a (+) and a (−) part, a state of affairs brought about by ionization within the molecule. Polar substances should have (1) large dielectric constant for steady fields ; (2) a dielectric constant decreasing rapidly as temperature rises ; (3) great dissociating power and tendency to cause ionization in gases. The polar substances are water, ammonia, sulphur dioxide, alcohols, etc. ; non-polar are hydrogen, oxygen, nitrogen chlorine, carbon dioxide, carbon tetrachloride, benzene, methane, etc. This classification agrees closely with that of De Broglie[45] for active and inactive balloelectric materials.

Summary.

We have cast our net over a wide area of research on the gas-liquid interface. Those sections of the subject giving the greatest yield are :—cataphoresis of bubbles, bubbling through liquids, drop-splitting, spraying, liquid jets, and waterfall effects. Of these six sections, all but the first are concerned with the measurement of the charges (called balloelectric) arising when a liquid/air surface breaks. From a digest of some ninety published Papers it is possible to state the following general principles :—

(1) As will be seen in the text above, highly conflicting results have been obtained by different observers using various methods for breaking a liquid surface. Methods so unlike in operation as waterfall and spraying of the same materials yield very different charges. Slight differences either in purity of material, or in the time of exposure to the gas of the surface to be broken, may account for this disparity in results.

Controversies rage even on the essentials of this subject up to the present time. No doubt progress would be quicker if investigators could agree to collaborate, using pre-arranged materials and apparatus.

(2) In balloelectric experiments no charge ever arises unless the liquid surface is rapidly increased or torn by the action of a gas, or solid, or other liquid.

When a solid rubs over another solid, as in a triboelectric process, those few molecules of the opposed surfaces which come into intimate contact combine completely, and are then torn asunder as the rubbing proceeds. This tearing process involves electrical separation, one surface gaining a net (—) charge, the other a (+) charge. When a liquid like mercury flows over a solid like glass it does not slide, but rolls, and again we have combination and rupture between opposed molecules, with electrical separation as before. But when a gas passes over a liquid the process is different. Combination occurs, but the gas lacks either the rigidity of a solid or the surface tension of a liquid to cause violent rupture of the surface with electrical separation. But if, as in balloelectric processes, the action of the gas is so violent that it tears apart the molecules of liquid, ions (—) make their escape into the gas, so that both it and the liquid acquire charges.

(3) There are three properties of a gas-liquid interface : Potential Difference, Surface Tension and Balloactivity, which are inter-related. Of these, the first two are definitely measurable ; the last is more difficult to define and measure.

We will attempt to correlate some established results as regards these three properties. Consider the action on water of certain materials :—

(*a*) Certain non-electrolytes (e.g., the alcohols) reduce the thermodynamic P.D., the electrokinetic P.D. and the surface tension, but increase the balloactivity. In like manner some oils (e.g., olive) reduce the thermodynamic P.D. and the surface tension, but greatly increase the balloactivity.

(*b*) Electrolytes, in small amount, reduce the electrokinetic P.D. in the case of multivalent (+) ions, and increase it in that of multivalent (—) ions ; they have little or no effect on surface tension ; they reduce, and in some cases reverse, the balloactivity.

(4) The double electric layer, which is the active ingredient of a bubble in cataphoresis, is not the only layer generating charges in balloelectric experiments. Other layers exist at and about the interface, and the amount of charge generated is a

measure of the suddenness and violence of the rupture of these and of the double electric layer, if existent.

(5) In balloelectric experiments, charges may be looked for either in the liquid or the gas. Of these, the gas phase yields much more detailed information as to charge, sign, and mobility of ions produced. But on measuring the ionic charges in the gas, since recombination of the (+) and (—) ions occurs, time is a factor to be considered. McClelland and Nolan, and others, have allowed for this time factor. An important generalization can be stated : Whereas for so many interfaces we find that the results given by the different balloelectric processes are in conflict with one another, in the case of distilled water/air the results are in qualitative agreement.

In this case the net charge in the air is found to be (—) for (*a*) Bubbling (Coehn and Mozer), (*b*) Drop Splitting (Simpson, Hochswender, J. J. Nolan), (*c*) Spraying (Christiansen, Eve, J. J. Nolan and Gill), and (*d*) Waterfall (Lenard, Kähler, Aselmann). The charge in the water in all these cases is (+).

(6) In researches on this subject temperature is one factor but little exploited so far. Vacuum is another, which has not been employed at all, to our knowledge. Yet in jets, waterfall and bubbling, if in no other cases, a vacuum on the interface is attainable at least in the important case of liquid mercury, and should profoundly influence balloelectric results. There remains a large field for investigation, especially in the direction of the comparison with identical solid, liquid and gaseous materials, of results obtained by the various methods coming within the purview of this Paper.

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References.

Section I.

(1) Kenrick. Zeitschr. fur physik. chemie, 19, 1896.
(2) Donnan. Brit. Ass. Address, Section B, 1923.
(3) Frumkin. Nature, August 2, 1924.
(4) Frumkin. Zeitschr. fur physik. chemie, 111, August, 1924.

Also the following :—

Freundlich Kapillarchemie, pp. 243, *et seq.* ; pp. 187, *et seq.*

Freundlich. The Physics and Chemistry of Colloids. General Discussion by the Faraday and the Physical Society of London (1921), pp. 146-149.

Section II.

(5) Coehn and Mozer. Ann. der Physik, 43, 1914.
(6) McLaughlin. Proc. Royal Dublin Soc., 17, 1922.
(7) McTaggart. Phil. Mag., February, 1914.
(8) McTaggart. Phil. Mag., September, 1914.
(9) McTaggart. Phil. Mag., 44, 1922.
(10) Alty. Proc. Roy. Soc., 106, 1924.
(11) Porter. Physics and Chemistry of Colloids, Faraday and Phys. Soc. Discussion (1921).
(12) Freundlich. Kapillarchemie, 1922 edn., p. 331, *et seq.*
(13) Mukherjee. Physics and Chemistry of Colloids (1921), Trans. Faraday Soc. (October, 1920).

(14) McBain. J. Phys. Chem., Vol. 28, 1924.
(15) Edser. Brit. Ass. Report, 1921.
(16) W. B. Hardy. Proc. Roy. Soc., Vols. 84, 86, 88, 100 and 101.
(17) Langmuir. J. Amer. Chem. Soc., 40, 1918.
(18) Adam. Proc. Roy. Soc., Vols. 99, 101, and 193.
(19) Evans and George. Proc. Roy. Soc., Vol. 103, 1923.
(20) Manley. Proc. Phys. Soc., Vol. 36 (4), 1924.
(21) Iredale. Phil. Mag., Vol. 48, 1924.

Also the following :—
Quincke. Pogg. Ann., 1861.

Section III.

(22) Alessandri. N. Cemento, 1902.
(23) Wolf. Beibl. Ann. der Physik., 29, 1905.
(24) Bloch. Ann. de chim. et de phys., 22 and 23, 1911.
(25) Rey. "Sur l'ionisation de l'air par les chutes d'eau," Gauthier Villiers, Paris, 1912.
(26) J. J. Nolan and Gill. Phil. Mag., 46, 1923.
(27) Kelvin, Maclean and Galt. Proc. Roy. Soc., February, 1895; Phil. Trans., 1898.
(28) Himstedt. Ann. der Physik., 12, 1903.
(29) Faraday. Experimental Researches, 1843.
(30) Blake. Wied. Ann., 19, 1883.
(31) Schwalbe. Wied. Ann., 58, 1896.
(32) Beggerow. Dissertation Freiburg, 1901.
(33) Gallarotti. R. Acc. dei. Lini, 1908.
(34) Henderson. Phil. Mag., 50, 1900.
(35) Holmgren. Proc. Physiogr. Soc. of London, 1894.

Section IV.

(36) Aganin. Ann. der Physik., 45, 1914.
Also the following :—
Lenard. Ann. der Physik., 1892.
J. J. Thomson. Phil. Mag., 1894.

Section V.

(37) Rayleigh. Proc. Roy. Soc., 194, 1879.
(38) Hiss. Dissertation Heidleburg, 1913.
(39) Burton and Wiegand. Phil. Mag., 23, 1912.
(27) Kelvin, Maclean and Galt. Phil. Trans., 1898.

Also the following :—
Rayleigh. Proc. Roy. Soc., 221, 1882.
Kaiser. Wied. Ann., 53, 1894.
Trubi. Dissertation Heidleburg, February, 1912.
Von Bernolak. Ann. der Physik., 39, 1912.
Freundlich. Kapillarchemie, 1922 edn., pp. 389-391.

Section VI.

(40) Lenard. Ann. der Physik., 1892.
(41) J. J. Thomson. Phil. Mag., 1894.
(42) Becker. Ann. der Physik., 29, 1909 ; 31, 1910.
(43) Aselmann. Ann. der Physik., 19, 1906.
(44) Kähler. Ann. der Physik., 12, 1903.

Also the following :—
Christiansen. Ann. der Physik., 51, 1916.
Elster and Geitel. Wied. Ann., 47, 1892.
Becker. Jahrbuch der Radioact, 9, 1912.
Lonsdale. Phil. Mag., 20, 1910.
Zwaardemaker and Hogewind. K. Akad. Amster. Proc., 22, 1920.

Section VII.

(45) De Broglie. Comp. Rend., 150, 1910.
(46) Bloch. Ann. de chim. et de phys., 22 and 23, 1911.
(47) Fischer. Wien. Ber., 11, 11a, 1902.
(48) Coehn and Mozer. Ann. der Physik., 43, 1914.
(49) P. J. Nolan. Phys. Rev., Vol. 18, 1921.
(50) Coehn and Duhme. Zeitschr. fur Physik., 26, 6, 1924.
(51) McClelland and P. J. Nolan. Proc. Roy. Irish Acad., 33, 1916.
(52) J. J. Nolan. Proc. Roy. Irish Acad., 33, 1916.

Also the following :—
Kosters. Wied. Ann., 69, 1899.
Wolf. Beibl. Ann der Physik., 29, 1905.
J. J. Thomson. Phil. Mag., 4, 1902.
Himstedt. Ann. der Physik., 12, 1903.
Bloch. Comp. Rend., 145, 1907.
De Broglie. Comp. Rend., 145, 1907.
De Broglie and Brizard. Comp. Rend., 150, 1910.
Lavoisier and Laplace. Phil. Trans., 1782.
Enwright. Phil. Mag., 29, 1890.
Townsend. Phil. Mag., 45, 1898.

Section VIII.

(53) Simpson. Phil. Trans., Vol. 209 ; Phil. Mag., 30, 1915.
(54) Lenard. Ann. der Physik., 47, 1915.
(55) Hochswender. Dissertation Heidleburg, July, 1919.
(56) J. J. Nolan. Proc. Roy. Soc., 90, 1914.

Also the following :—
Lenard. Met. Zeitschr., 21, 1904.

Section IX and General Theories.

(57) Christiansen. Ann. der Physik., 40, 1913 ; 51, 1916.
(58) Traube. Ann. der Physik., 62, 1920.
(59) Eve. Phil. Mag., 14, 1907.

(60) J. J. Nolan and Enright. Proc. Roy. Dublin Soc., 17, 1922.
(61) J. J. Nolan and Gill. Phil. Mag., 46, 1923.
(62) Rayleigh. Proc. Roy. Soc., 47, 1890.
(63) De Noüy. Phil. Mag., 48, 1924.
(64) Harkins. J. Amer. Chem. Soc., 39, 1917.
(65) J. J. Thomson. Phil. Mag., 27, 1914.

Also the following :—
Bloch. Comp. Rend., 150, 1910.
Pomeroy. Phys. Rev., 27, 1908.

DISCUSSION.

Dr. P. E. Shaw (communicated remarks) : I regret that I cannot attend this meeting. The usefulness of studying the liquid-gas interface, as we have tried to do, appears when we contrast it with the old and troublesome case of the solid-solid interface. Consider a case : Glass-cotton. The surface of each of these solids is strained with a tension tangential, and a pressure, normal to the surface. These strains are indeterminate, they vary with depth from the geometrical surface, and depend on the recent physical treatment and on the action of chemicals used in their cleaning. Above the surfaces of each solid are films many molecules thick, formed by gases, especially water vapour, condensed from the air. In the films themselves are ions proceeding from the solid, which, according to Knoblauch's theory, play a preponderating part in producing electric charges when contact occurs. In addition, the films contain any impurities which may have accumulated on the surfaces. In fact, each solid surface, owing to its attractive forces, becomes a natural dumping ground for any solid, liquid or gaseous materials, which may come near it. If we bring the glass and cotton into contact, the electrical separation which now occurs depends not only on the surfaces themselves, but also on the mechanical pressure applied and on the gas pressure existing at the time. If, further, the surfaces are rubbed together heat is generated, the temperature of each surface changes differently ; the chemical and physical conditions change, and the charges produced vary accordingly. Thus, the surface of a solid is a particularly unfavourable ground for investigation. We have a great number n of unknown factors, and to solve our problem of the genesis of charges, we require n equations. It becomes hopeless to frame a theory until we have acquired a vast amount of data derived from experiments with n changes of the physical and chemical factors involved. But now turn to the liquid-gas case, say, water-air. Both materials can be easily cleaned and renewed, the film trouble is slight or non-existent, and the strain conditions, occurring on the liquid only, are constant and ascertainable. So this interface is relatively easy to investigate. Yet even for this simple liquid-gas case the results gleaned so far are meagre, considering the great number and variety of researches which have been undertaken. But at least one great law emerges, viz., that electrons are liberated from a liquid surface whenever it is violently torn by an alien gas. Interface problems will assuredly bulk very large in the immediate future ; and I think the soundest way to approach the difficult cases is by way of the simple ones, such as the liquid-gas and the solid-gas.

Prof. A. M. Tyndall : The subject is full of interesting problems, solutions of which do not seem possible at present. For instance, when air is bubbled through water, many ions are formed, but bubbles of steam from boiling water give none. Mr. V. J. Long, in my laboratory, has recently noticed that neither water nor liquid air boiling violently in an open dish produce any ions. It is difficult to see how any theory which does not introduce the gas phase as an important factor could explain this. Are the authors aware of Aitken's modification of Rayleigh's impinging jets experiment ? It is well known that slight electrification causes the jets to coalesce. Aitken has shown that jets of hot water coalesce without the aid of electrification. Possibly the reduction in the adsorbed layer of air at the higher temperature is the cause of this. If so, could electrification influence the adsorbed content of gas in the same way ?

Prof. F. L. Hopwood : It has been shown by Trouton that in the limiting case of a bubble moving through a tube under gravity and filling it the speed is independent of the size of the bubble. Such bubbles have ripples on their surface (investigated also by Gibson), and possibly these ripples if they occur on smaller bubbles might cause the departure from theory mentioned by the author in describing McTaggart's experiments.

Reply to the discussion by Mr. H. W. GILBERT :—In reply to Prof. A. M. Tyndall : As we have noted in the Paper, in all cases when balloelectricity is produced the two phases must differ chemically. Thus, J. J. Thomson showed in 1894 that drops falling through their own vapour produced no balloelectricity, and many other workers have shown similar negative effects for bubbling and boiling processes. This evidence constitutes one of the great objections to Lenard's theory, which ascribes a negligible effect to the gas phase. The explanation of Aitkin's phenomenon may be that at the higher temperature we have a reduced surface tension. Rayleigh has shown that the presence of a minute amount of grease or dust will cause coalescence of the bouncing jets. However, as suggested by Prof. Hopwood, the adsorbed layer of air is also an important factor. It might be possible to test it by some modification of the method used by Palmer to investigate adsorption films on metals (Proc. Roy. Soc., July, 1924). In reply to Prof. F. L. Hopwood : The effect noticed by Gibson and Trouton may be present in cataphoretic experiments like those of Quincke, where the bubble nearly fills the tube. With the small bubbles moving very slowly along the axis of a tube of diameter many times their own the effect would be very slight.

XIX.—A CONTACT THEORY OF DIELECTRIC ABSORPTION AND POWER LOSSES.

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Abstract.

A simple explanation is proposed of absorption, residual charge, and allied phenomena, in solid dielectrics. In accordance with classical theory, the dielectric is assumed to possess a certain true capacity, defined by its dielectric constant, and a certain conductance, here considered as probably electrolytic in type. The so-called anomalous properties are considered to be due to the properties of the contact surfaces of the dielectric and its metal electrodes. These contact surfaces appear to offer great resistance to the passage of ions or electrons across them, so that when an E.M.F. is applied to a condenser there is an accumulation of charges at the surfaces. These charges constitute the absorbed and residual charges. The experimental evidence in favour of this hypothesis is reviewed.

The behaviour of each contact surface is such that it may be represented by a large capacity in parallel with a high resistance, and thus a capacity-resistance combination is suggested, which is equivalent to an actual condenser. The properties of this combination are considered mathematically with reference to the experimental laws of absorption, and power losses in alternating fields, and the extent to which the theory is capable of explaining the experimental results is pointed out. The bearing of the theory on dielectric measurements under various conditions is also discussed.

I. Introductory.

SOME time ago Mr. D. W. Dye and the author made a series of measurements on the dielectric properties of insulating materials in thin sheet form, using two different methods: (1) The change in capacity produced on inserting the material in the air gap between two parallel metal plates was measured; (2) Mercury electrodes were applied to the two sides of the sheet under test, and the capacity of the condenser so formed was measured. Values of the dielectric constants of the materials calculated from the results of these observations by the usual formulæ showed systematic discrepancies, the mercury electrode method always giving the higher result. In order to explain these discrepancies, the writer put forward the suggestion that there was a contact effect at the mercury dielectric surface—e.g., a "polarisation capacity" effect such as occurs in electrolytes. We have considerable reason to believe that the discrepancies quoted in our paper on mica[1] are largely due to slight irregularities in the construction of the air gap; but experiments made on varnished cloth did not seem to be sufficiently explained by these irregularities, and led to the examination of the possibilities of the contact effect suggested above. It now appears that such an effect is capable of explaining many of the anomalous properties shown by dielectrics, and it is proposed to show in this Paper how the phenomena of the polarisation of dielectrics under a constant electrostatic field (i.e., the so-called absorption phenomena), the residual charge, and the power loss in alternating fields are all capable of explanation in terms of conduction, electrolytic in type, in the body of the insulating material associated with what may be described as a contact capacity effect at the surface.

II. Polarisation in Constant Fields.

According to Maxwell's theory, the electric actions occurring in any material are characterised by two constants, the specific conductivity of the material and its specific inductive capacity or dielectric constant. If an electrostatic field of strength F is applied to a substance, electric displacement of two kinds is produced :—

(*a*) There is a continuous movement of electricity in the direction of the applied field. If σ is the specific conductivity of the material, then the quantity of electricity crossing each unit of area of the substance (the area being measured at right angles to the flow) in each unit of time is given by $F\sigma$. This displacement of electricity continues at this constant rate as long as the field F is maintained.

(*b*) Another kind of electric displacement is also produced. This does not increase indefinitely with time, but almost instantly reaches its final value of $KF/4\pi$, where K is the dielectric constant of the material.

At the present time we associate the electric displacement of the first kind with the free electrons in the material, and that of the second type with the electrons which are bound by " elastic " forces to the fixed nuclei of the atoms or molecules.

It is a matter of common knowledge, however, that when a condenser is made by applying metal electrodes to any dielectric which is partly or wholly solid, and an E.M.F. is applied to these electrodes so as to maintain a constant potential difference between them, the actual electric displacement occurring is not simply that indicated by this simple theory. What is actually observed is—

(1) A comparatively large instantaneous* electric displacement. This is considered to be the Maxwellian displacement $KF/4\pi$.

(2) A further electric displacement, not at a uniform rate such as would identify it as the displacement due to conductance $\int F\sigma dt$, but at a rate which decreases with time, rapidly at first but afterwards more slowly, until finally (after many hours or even months) the rate of displacement becomes very small and constant, so that it is then assumed to be the conductance displacement, and is used to determine the constant σ. In other words, what is actually observed is—

(1) The true capacity charge, regarded as instantaneous.
(2) The " absorption " current, which gradually diminishes to zero, leaving only
(3) The leakage current.

The simple classical theory further says that when the field F is removed the displacement $KF/4\pi$ vanishes, and the conductance displacement ceases—i.e., there is an instantaneous displacement $-KF/4\pi$, which is the collapsing of the capacity displacement caused by the initial application of the field, and is thus in the opposite direction to the original displacement, and no further conductance displacement takes place. Thus the displacement due to capacity is regarded as reversible ; that due to conductance is not. In practice, if the condenser which

* Following the usual custom in discussing dielectric anomalies, the actual electric displacement is regarded as consisting of two portions, one being regarded as instantaneous, and the other being a function of time. This division is, of course, quite arbitrary, and is simply adopted as a matter of convenience. An exact specification of the " instantaneous displacement " is probably impossible. A masterly discussion of the matter has been given by Hopkinson, Phil. Trans., Vol. 189, p. 109 (1897).

we have imagined to be charged is short circuited by connecting its plates together by means of a wire, what is observed is—

(1) An instantaneous displacement equal in magnitude to the original instantaneous displacement, but of opposite sign.

(2) A further displacement also in the opposite direction to the original displacement. This occurs at a rate which is rapid at first, but which gradually decreases down to zero.

In other words, we observe the true capacity discharge, regarded as instantaneous, followed by the residual discharge current, which gradually decreases down to zero, leaving the condenser entirely uncharged. If, however, the condenser is open circuited (i.e., the wire connecting its plates together is removed) before the discharge is complete (and this may take hours or days), a charge gradually builds up on the electrodes or plates of the condenser. This is known as the residual charge, and is of the opposite sign to the charge taken by the condenser during the time the voltage is applied.

Several theories have been put forward in order to explain these anomalous charging and discharging currents in a dielectric—i.e., currents or electric displacements which are apparently independent of the conductance σ and the dielectric constant K. Maxwell showed that they can be explained without any extension of the simple theory if the dielectric be assumed to consist of layers of materials of different properties, so that σ/K is different for different layers. This explains the existence of the phenomena in the case of a cable with a laminated dielectric; but H. A. Wilson[2], Thornton[3] and S. W. Richardson[4] have found the same effects in crystalline quartz and iceland spar, and it is difficult to believe that such substances are not of homogeneous structure in any particular direction. Von Schweidler[5] has advanced the theory that a dielectric possesses in addition to the displacement electrons, which are capable of vibratory motion about their equilibrium position with a definite natural period and definite damping, other ions in which the damping is so great that their motion is aperiodic. These ions move very slowly under the influence of an applied field, and thus give rise to the anomalous charging current. The anomalous discharge and the residual charge are of course considered to be due to their slow return to their original equilibrium positions. Unlike Maxwell's theory, this assumes that the dielectric actually possesses other properties than those characterised by σ and K, a complication which one would prefer to avoid if possible. Thornton[3] has supposed that the anomalous displacement is due to a further motion of the displacement electrons, due to inter-attractive forces consequent upon their initial displacement by the applied field. It is, however, difficult to see why this further displacement should take place so slowly and why it should exceed in amount the displacement predicted by the Lorentz theory of dielectrics, which it must do, if it is to explain the observed facts.

The theory now proposed is as follows: The dielectric is assumed to possess the two properties defined by K and σ only. Thus it possesses a definite capacity and a definite conductance. The conductance is considered to be electrolytic in type. In Fig. 1 let AB represent two metal electrodes applied to a slab of dielectric. In practice the metal will probably never actually make true contact with the dielectric, such contact as one gets in a soldered joint, for example. In the diagram therefore, a small gap is shown between the dielectric faces CD and the metal faces AB. Now suppose A and B are connected to a battery so as to maintain a constant

potential difference between them. The first consequence is that a potential gradient is set up in the dielectric and thus a definite displacement proportional to the dielectric constant of the material K is produced. This is the normal charge. Now, as a consequence of the potential gradient in the dielectric, the ions begin to move so as to produce a current proportional to its conductance. The positive ions move towards C, say, and the negative ones towards D. Corresponding to this current in the dielectric, there must of course be a movement of free electrons in the connecting leads to A and B. Thus we have a further accumulation of negative electrons at A, whilst positive charges preponderate still further at B, as shown. The theory now supposes that these ions at the contact faces find great difficulty in crossing over from dielectric to metal, and opposite charges continue to accumulate. It is obvious that these charges at C and D cause a back E.M.F. in the dielectric, which tends to stop this current. Thus, this so-called anomalous current, or absorption current, gradually gets smaller and smaller, until finally the number of ions moving up to C and D is only equal to the numbers which can cross the contact

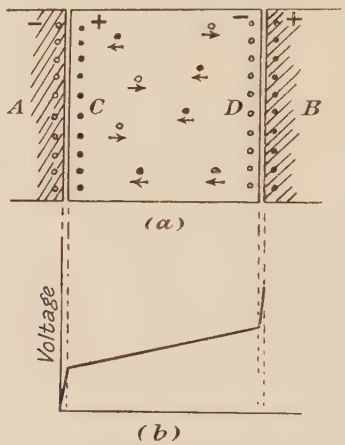

FIG. 1.—DIAGRAMMATIC REPRESENTATION OF A DIELECTRIC WITH METAL ELECTRODES.

face. This is the current which is usually regarded as the true leakage current. According to this theory, when the condenser has reached this steady state (and thus from the usual point of view is fully charged) the actual potential gradient in the dielectric is comparatively small, and therefore the true dielectric displacement is small. The charge on the contact faces may, however, be very great, and this is considered to be the "absorbed charge." The voltage distribution in this case is shown in Fig. 1 (*b*).

Consider now the phenomena of discharge. Let the plates AB be connected by a wire so as to equalise their potentials. Let V be the voltage applied to A and B in the first case, and let x be the thickness of the dielectric, and $x+\delta x$ the effective distance between A and B—i.e., the effective thickness of the dielectric when allowance is made for the imperfect electrode contact. When the condenser is charged, let P be the back E.M.F. due to the accumulation of ions round C and D, then the resultant voltage gradient in the dielectric is $\frac{V}{x+\delta x}-\frac{P}{x}$, and the true dielectric dis-

placement is $\frac{K}{4\pi}\left(\frac{V}{x+\delta x}-\frac{P}{x}\right)$. On short circuiting, V is reduced to zero, and thus the voltage gradient becomes $-\frac{P}{x}$, and the true dielectric displacement $-\frac{K}{4\pi}\cdot\frac{P}{x}$. Thus the change of displacement on short circuiting is $-\frac{K}{4\pi}\left(\frac{V}{x+\delta x}\right)$. This is seen to be equal to the instantaneous charge on applying the voltage V, and thus agrees with experiment. The surprising conclusion arrived at, however, is that this instantaneous discharge, although equal to the instantaneous charge, is not merely the collapsing of this charge. In fact, instead of becoming discharged on short circuiting, the dielectric becomes charged or polarised in the opposite direction by the back E.M.F. due to the ions at the contact surfaces. Another effect of this E.M.F. is that now the ions begin to move in the opposite direction, thereby causing the "anomalous" discharge current. The greater the extent of this motion the smaller becomes the back E.M.F. of the ions, and thus this current gradually decreases down to zero. If the external circuit is not kept closed, the movement of the ions away from the contact surfaces liberates corresponding charges in the electrodes, and as these charges cannot flow along the connecting wire and so neutralise each other, there is an accumulation of electricity on the condenser plates. This is the residual charge. It may be large enough to raise the condenser plates to quite high voltages.

Curie[6] and S. W. Richardson[4] have discussed their observations on dielectrics in terms of an "internal E.M.F. of polarisation." On the present theory this is simply the back E.M.F. due to the accumulation of ions at the contact faces. Richardson made measurements of the E.M.F. by means of a potentiometer arrangement. He found that P, the internal E.M.F. of polarisation, increased with the time of charging, rapidly at first, but afterwards more slowly, which is, of course, exactly what is to be expected by the theory.

III. The Equivalent Capacity-Resistance Combination.

It is to be noted that the metal-dielectric contact surface behaves like a large condenser, and according to this ionic theory, these "contact condensers" must be supposed to possess very high resistance. Thus we may represent the actual condenser by the combination of perfect condensers and resistances shown in Fig. 2. Here C_1 represents the true capacity of the dielectric, and R_1 is its true resistance, C_A and C_B are the contact capacities, and R_A and R_B the contact resistances. In all dielectrics in which the "absorption current" greatly exceeds the leakage current we must suppose that the true resistance of the dielectric is much less than the contact resistances.

When this theory was first conceived this assumption was so contrary to current notions that it appeared to be a very serious objection. It means, for example, that if two samples of the same dielectric, but of different thickness, are taken and placed between metallic electrodes (tin foil or mercury, etc), and their resistances are measured in the usual way, then, in spite of the differences in thickness, the resistances will be very nearly the same, since nearly all the resistance lies in the contact surfaces. There seemed to be no experimental evidence for this, and all determinations of the specific resistance of dielectrics tacitly assume that such is

not the case. Quite recently, however, H. M. Barlow[7], following a totally different line of investigation, has arrived at the same conclusion—at least for certain insulating materials used in practice. Barlow was investigating the frictional forces between sliding surfaces across which a direct current was flowing. He found that when one of the substances in contact was a metal, and the other a comparatively poor insulator, such as slate, celluloid, red fibre, or lithographic stone, the passage of a current across the contact caused a considerable increase in the frictional force between the surfaces. He traced this to an increase in the normal pressure between the surfaces due to the fact that nearly the whole of the potential drop between the two substances was located at the contact surface—i.e., the contact resistance was enormously greater than the body resistance. In other words, the increase of normal pressure is due to the attractive force between opposite charges, which accumulate on either side of the contact surface, exactly as the present theory indicates. These poor insulators naturally show the effect to a much greater extent than the best dielectrics. Barlow did not detect it in the case of glass, ebonite, or micanite ; but in such cases the surface charges would take hours to reach anything approaching their maximum values, and the effect might very easily escape detection on this account. Barlow also quotes some results of Addenbrooke[8] for the direct-current resistivity ρ of celluloid obtained by measurements on sheets of different thickness, using mercury electrodes. Different values are obtained for different thicknesses, in fact ρ is very nearly inversely proportional to the thickness, which again points to the fact that the bulk of the resistance is in the contact face. Barlow himself made measurements of a similar nature on slate and lithographic stone, with the same result. Further, the work of Richards[9] shows that charges of opposite sign can exist on either side of a contact surface of metal and dielectric, even when these surfaces make wringing contact, each surface being flat to half a wave-length of sodium light. Richards measured these charges in the case of contacts of glass, quartz, fluorite and ebonite with steel. (In this case the charges were produced merely by wringing the surfaces together, and thus they may be of a different nature from those produced as a result of the application of an external E.M.F.)

In view of all this, we see that the assumptions required by the present theory are not without some experimental foundation.

IV. Some Practical Considerations.

It has been remarked that the contact surface of metal and dielectric may be regarded as acting like a large condenser of high resistance, and that in practice a condenser may be represented by the combination of ideal capacities and resistances shown in Fig. 2. Consider now some of the simplest properties of the system, and it will be found that many obscure phenomena met with in practice are easily explained.

(*a*) *A.C. and D.C. Resistance.*—It is a well-known fact that the alternating-current resistance of a dielectric is enormously less than the direct-current value. By reference to Fig. 2 it is at once seen that the D.C. resistance is $R_1+R_A+R_B$, since the final constant leakage current must traverse these three resistances. If now alternating voltage is applied, the current can cross the surfaces as a capacity current through the condensers C_A and C_B, and since their impedances at the frequencies met with in practice are much less than those of R_A and R_B, the current (R.M.S.) passing in this case for a given applied voltage (R.M.S.) is much greater than the current

flowing when unidirectional voltage of the same magnitude is applied. This current now divides between R_1 and C_1, and since R_1 is much less than R_A, the portion passing through R_1 is quite considerable, the actual amount depending on the frequency. Thus the power dissipated in the resistance R_1, with a given applied voltage, is far greater for A.C. than for D.C. Thus may arise the so-called dielectric hysteresis loss, as a consequence of which the effective A.C. resistance is much less than the effective D.C. resistance, though, according to the present theory, if the true resistance R_1 could be measured it would be the same in both cases.

(*b*) *The Absorbed Charge.*—When measurements of the so-called absorbed charge are made, the most astonishing point is its enormously high value—e.g., in an experiment made by the writer, a sample of varnished cloth with mercury electrodes was charged for about 48 hours with a constant voltage. The electrodes were then short circuited, and the residual discharge current measured during the next 48 hours. The total charge coming out in this time (obtained from the time integral of the current) was such as would correspond to a dielectric constant of 700 for the sample. The measured dielectric constant at 800 ~ was 4·7. Thus the absorbed charge must be hundreds of times greater than the true capacity charge.

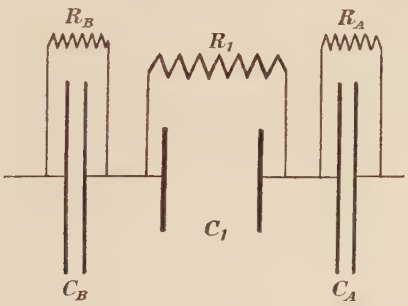

Fig. 2.—Network Equivalent to an Imperfect Condenser.

This is explained by the enormous values of the contact capacities C_A and C_B compared with C_1. When the final steady state is reached the potential drop across C_A and C_B is considerable, owing to the high values of R_A and R_B, and thus these condensers possess very large charges, which are slowly released as the discharge proceeds.

V. Approximate Mathematical Theory.

Before using the model of Fig. 2 for the purpose of calculation it is necessary to note the assumptions involved. It means that the back E.M.F. due to the accumulation of ions at the surfaces is proportional to the total accumulation of charge of either sign—e.g., the back E.M.F. at surfaces $AC = M\int idt$, where $M = \frac{1}{C_A}$ and $\int idt$ is the total charge conveyed to the surface C by the positive ions moving up to it (Fig. 1). If now the direction of the applied E.M.F. be reversed, then negative ions will move up to the surface C, and in this case we have the back E.M.F. $= M'\int idt$. The contact capacity is now $C_A' = \frac{1}{M'}$. It is not necessarily the same as in the previous

case, since it may depend on the size of the ions moving up to the surface, and the positive and negative ions may not be of the same size. Similarly, the new contact resistance R_A' may have a different value from R_A, since the positive and negative ions may not move with the same velocity under the action of a given force. The same thing may also occur at the other contact surface, so that when the condenser is carrying alternating current the values of the contact resistances and capacities may also alternate. As a first approximation we shall, however, make the assumption that the contact resistances and capacities are constant for varying applied E.M.F.'s, and, further, that they are the same at the two surfaces—e.g., suppose we are dealing with a parallel plate condenser, the electrodes being of the same size and of the same metal, then by symmetry the two surfaces may be regarded as possessing identical properties.

In Fig. 2 let V_A be the potential differences across C_A, V_1 that across C_1, and V_B that across C_B. Let I be the total current in the circuit. Then

$$I=\frac{V_A}{R_A}+C_A\frac{dV_A}{dt}=\frac{V_1}{R_1}+C_1\frac{dV_1}{dt}=\frac{V_B}{R_B}+C_B\frac{dV_B}{dt}$$

Also, if V is the total potential difference across the condenser

$$V=V_A+V_1+V_B$$

If now we assume $C_A=C_B=2C_0$, and $R_A=R_B=\frac{1}{2}R_0$, then $V_A=V_B=\frac{1}{2}V_0$ (say), and the above equations reduce to

$$I=\frac{V_1}{R_1}+C_1\frac{dV_1}{dt}$$

$$I=\frac{V_0}{R_0}+C_0\frac{dV_0}{dt}$$

$$V=V_1+V_0$$

Here C_0 may be regarded as representing the total contact capacity effect, R_0 the total contact rsistance effect, and V_0 is the total surface voltage drop. These equations are seen to be of exactly the same form as those given by Maxwell's theory of a stratified dielectric when only two layers are considered. The general solution has been given in a convenient form by Meyer[10]. It may be written

$$I=C\frac{dV}{dt}+\frac{V}{R}+\frac{kC}{T}e^{-\frac{t}{T}}\int_{-\infty}^{t}e^{\frac{t}{T}}\frac{dV}{dt}dt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$C=\frac{C_1C_0}{C_1+C_0}$$

$$R=R_1+R_0$$

$$T=\frac{R_1R_0(C_1+C_0)}{R_1+R_0}$$

$$k=\frac{(R_1C_1-R_0C_0)^2}{C_1C_0(R_1+R_0)^2}$$

Consider now the cases of most importance in practice.

1. Let a constant voltage E be applied at the instant $t=0$. Then the current is given by

$$I=\frac{E}{R}+E\frac{kC}{T}e^{-\frac{t}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It may be regarded as consisting of two parts, the leakage current $\frac{E}{R_1+R_2}$, and the "after effect" or absorption current$=E\frac{kC}{T}e^{-\frac{t}{T}}$, which decays exponentially with time, approaching a zero value as the value of t becomes very great.

Suppose now that having kept the applied voltage constant for a time interval t_1, it is reduced to zero by short circuiting the condenser. In the interval $t=0$ to $t=t_1$ the current is given by (2). For values of t greater than t_1 it is given by

$$I=\frac{kC}{T}e^{-\frac{t}{T}}\left[E-Ee^{\frac{t_1}{T}}\right]$$

$$=\frac{EkC}{T}e^{-\frac{t}{T}}-\frac{EkC}{T}e^{-\frac{(t-t_1)}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The first term in this expression is smaller than the second, thus the current is now in the opposite direction. Further, the relation between this residual discharge current and the anomalous charging current is exactly that stated in Hopkinson's Superposition Principle[11], which was in agreement with his experimental results.

If the applied voltage E is kept constant for an indefinitely long time, then by integration we see that the total absorbed charge is EkC. If then the condenser is short circuited, the residual discharge current, if t is now measured from the instant of short circuit, is given by $-E\frac{kC}{T}e^{-\frac{t}{T}}$ i.e., the residual discharge current is given by exactly the same expression as was the original absorption current, and if this current is allowed to flow for an indefinitely long time the total charge conveyed by it is $-EkC$—i.e., the absorbed charge is reversible as regards quantity of electricity flowing (though not as regards energy). These relations are borne out by experiment[12].

The term $C\frac{dV}{dt}$ in the general expression for the current through the condenser (1) has not yet appeared in this discussion. It of course represents the instantaneous charge or discharge. C is the "geometric capacity" of the condenser. It differs slightly from the true capacity of the dielectric C_1, on account of the surface capacity C_0, but when C_0 is large (which must be the case if the electrodes make good contact with the dielectric), C and C_1 are practically identical.

With regard to the magnitude of the absorption current, we see that it is directly proportional to the applied voltage and also to $\frac{kC}{T}$. Substituting we find that

$$\frac{kC}{T}=\frac{\left(1-\frac{R_1C_1}{R_0C_0}\right)^2}{R_1\left(1+\frac{R_1}{R_0}\right)\left(1+\frac{C_1}{C_0}\right)^2}$$

which reduces to $1/R_1$ when R_0 and C_0 are so large compared with R_1 and C_1 that the ratios $\frac{R_1}{R_0}$ and $\frac{C_1}{C_0}$ are negligible compared with unity.

Thus in general the smaller the value of R_1 the larger will be the absorption current. This accounts for the rapid increase in the absorption current with rise of temperature.

2. Suppose the applied voltage is alternating and of sine wave form, so that it may be represented by

$$V=V_0e^{j\omega t}$$

where frequency$=\frac{\omega}{2\pi}$

Then the expression for the current becomes

$$I=V\left[j\omega C+\frac{1}{R}+j\frac{\omega kC}{1+j\omega T}\right]$$
$$=V\left[j\omega\left(C+\frac{kC}{1+\omega^2T^2}\right)+\frac{1}{R}+\frac{\omega^2kCT}{1+\omega^2T^2}\right]$$

Thus the effective capacity of the condenser at the frequency $\frac{\omega}{2\pi}$ is

$$C_e=C+\Delta C=C+\frac{kC}{1+\omega^2T^2} \quad \ldots\ldots\ldots \quad (4)$$

where $\triangle C$ is the increase of capacity due to "absorption," and the effective conductance is

$$G=\frac{1}{R}+\frac{\omega^2kCT}{1+\omega^2T^2} \quad \ldots\ldots\ldots\ldots \quad (5)$$

The loss angle δ is given by

$$\frac{C+\Delta C}{C}\tan\delta=\frac{\omega kT}{1+\omega^2T^2}+\frac{1}{RC\omega} \quad \ldots\ldots\ldots \quad (6)$$

The way in which these quantities vary with the frequency is shown in Fig. 3. The effective conductance, and therefore the power loss, is much greater for A.C. than for D.C., and this power loss increases rapidly as the frequency increases. The various functions are of exactly the same form as those given by Maxwell's theory.

VI. Comparison with Experimental Results.

When the formulæ given by this approximate theory are compared with the results of experiments, it is found that, although the capacity, power loss and absorption current vary with time or frequency in a manner which may be roughly represented by the formulæ, the agreement is by no means perfect—e.g., the absorption current for a constant impressed voltage decays rapidly with time, but the actual law of the decay is not a simple exponential one. Similarly, although the capacity and power factor (sin δ, which is practically the same as tan δ) in general both increase as the frequency decreases, the laws are not exactly those shown in Fig. 3. This of course may be explained by the fact that the assumptions made are

known to be only approximately fulfilled. As a first approximation we have represented the contact effects by a single capacity C_0 with shunt resistance R_0. We have shown above that they could be better represented by two different capacities C_A C_B, with corresponding resistances R_A R_B (Fig. 2). In this case the equations are of the same form as those for Maxwell's theory of the stratified dielectric with three layers[10]. The general solution is found to be of the form

$$I=C\frac{dV}{dt}+\frac{V}{R}+\frac{k_1C}{T_1}e^{-\frac{t}{T_1}}\int_{-\infty}^{t}e^{\frac{t}{T_1}}\frac{dV}{dt}dt+\frac{k_2C}{T_2}\int_{-\infty}^{t}e^{\frac{t}{T_2}}\frac{dV}{dt}dt.$$

where

$$\frac{1}{C}=\frac{1}{C_1}+\frac{1}{C_A}+\frac{1}{C_B}$$

$$R=R_1+R_A+R_B,$$

and k_1 k_2 T_1 T_2 are constants similar to those in (1), their values depending on

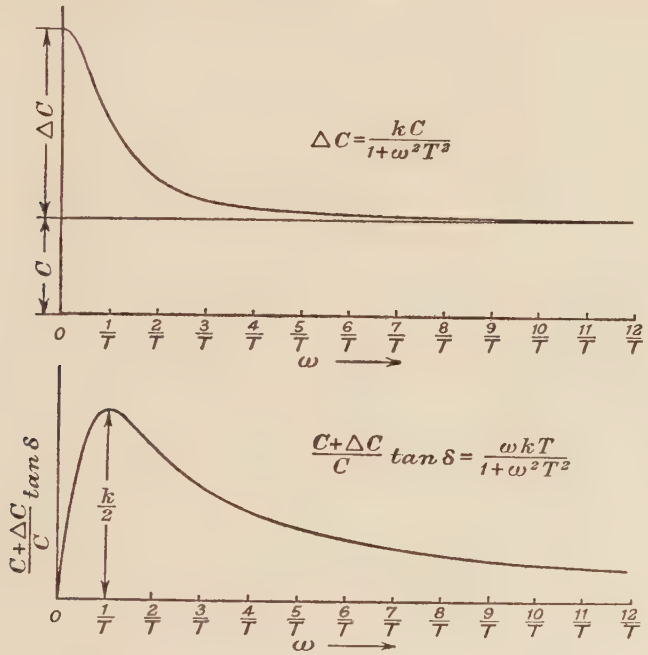

FIG. 3.—VARIATION OF CAPACITY AND LOSS ANGLE WITH FREQUENCY.

the values of C_1 C_A C_B R_1 R_A and R_B. Thus the function representing the decay of the absorption current now contains two exponential terms. The increment of capacity due to absorption is given by

$$\Delta C=\frac{k_1C}{1+\omega^2T_1^2}+\frac{k_2C}{1+\omega^2T_2^2},$$

whilst the expression for loss angle due to absorption is

$$\tan\delta=\frac{C}{C+\Delta C}\left\{\frac{k_1\omega T_1}{1+\omega^2T_1^2}+\frac{k_2\omega T_2}{1+\omega^2T_2^2}\right\}$$

These expressions are capable of representing the experimental results with greater accuracy than the simpler expressions, though, as they are not convenient in use, they are not of much practical importance.

Almost all the theories which have been advanced to explain dielectric anomalies have given expressions of this form—*cf.* those of Maxwell, Pellat, Schweidler. In order to explain the observed facts, Schweidler[5] expressed the absorption current as a function of time by an infinite series of exponential terms, whilst Wagner[13] showed that nearly all the observations could be explained by supposing the time constants of the exponential terms were grouped about certain most probable values, according to a distribution law based on the laws of probability. It is easy to see that the present theory would require extension on the same lines if any set of experimental results were to be explained quantitatively. The contact effects at each electrode have been represented by an ideal condenser, together with a shunt resistance. This can only be a rough approximation. The " double layer " at each electrode is not likely to be of uniform thickness, and thus the surface of the dielectric itself will not be an equipotential surface. Surface conduction will therefore play a small part at least. Further, each element of the contact surface must be regarded as a small condenser with its appropriate resistance, the values changing from point to point over the surface. Each element may give rise to an exponential term in the absorption current time function, and thus this function may be regarded as consisting of a series of exponential terms of varying time constant, the actual value of the time constant depending on the particular element of contact surface concerned. Further, it is quite probable that at any one electrode there would be a certain most probable value of contact capacity and resistance for any element of the contact surface. At the other electrode there might be a similar probable value. Thus the exponential terms in the expression for absorption current might be expected to be grouped about one or two probable values.

Wagner[14] has shown that functions of this form are capable of representing observations he has made on a very wide range of insulating materials. The expressions are of course very complicated, and not at all suitable for calculation in practice. They will not, therefore, be reproduced here. Their value merely lies in the fact that they show how the very complicated results observed in practice may be explained in terms of a theory which in its physical aspect is comparatively simple.

VII. The Air Gap and Mercury Electrode Methods.

Experiments on dielectrics are usually made under one of two conditions :—

(1) Metal electrodes are pressed into contact with the dielectric ; or
(2) The dielectric is placed in an air gap between two electrodes.

It may be worth while to examine the two methods in the case of most practical importance (alternating current), in the light of the present theory. In each case we have the dielectric, which we shall consider as a capacity C_1 with shunt resistance R_1, in series with another condenser C_0. In case (1), C_0 is the contact capacity ; in case (2) it is the capacity of the part of the air gap not occupied by the dielectric. We shall suppose the contact resistance R_0 to be infinite. This seems reasonable in the case of the air gap, and in the case of mercury electrodes absorption effects are

usually enormously greater than " true leakage," so that the supposition is probably justifiable. Let us consider the capacity at frequency $\omega/2\pi$. We have

$$\text{Capacity}=C+\Delta C=C+\frac{kC}{1+\omega^2T^2}$$

$$\text{where } k=\frac{C_0}{C_1},\ T=R_1(C_1+C_0),\ \text{and } C=\frac{C_1C_0}{C_1+C_0}$$

$$\therefore \text{ effective capacity}=\frac{C_1C_0}{C_1+C_0}\left[1+\frac{C_0}{C_1}\cdot\frac{1}{1+\omega^2R_1^2(C_1+C_0)^2}\right] \quad . \quad . \quad . \quad . \quad (7)$$

This represents the observed capacity of the sample in terms of the true constants of the material. Now take the case of the air-gap method. Denote the capacity as measured by this method by C_g. In using the simple formula for this method we put

$$\text{Observed capacity}=\frac{C_gC_0}{C_g+C_0}$$

Equating this with the above expression we find

$$\frac{C_g}{C_g+C_0}=\frac{C_1}{C_1+C_0}\left[1+\frac{C_0}{C_1}\cdot\frac{1}{1+\omega^2R_1^2(C_1+C_0)^2}\right]$$

$$=\frac{C_1}{C_1+C_0}\ [1+\alpha] \text{ say} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From this it is obvious that the calculated value C_g is higher than the true capacity of the sample C_1, the difference depending on the factor α. Equation (8) may be written

$$C_g=\frac{C_1(1+\alpha)}{1-\frac{C_1}{C_0}\alpha}=\frac{C_1\left[1+\frac{C_0}{C_1}\cdot\frac{1}{1+\omega^2R_1^2(C_1+C_0)^2}\right]}{1-\frac{1}{1+\omega^2R_1^2(C_1+C_0)^2}}$$

Put $\frac{C_0}{C_1}=z$. Then

$$C_g=\frac{C_1\left[1+\frac{z}{1+(1+z)^2\cot^2\delta}\right]}{1-\frac{1}{1+(1+z)^2\cot^2\delta}}$$

where δ is the true loss angle of the material—i.e., $\cot\delta=R_1C_1\omega$.

This reduces to

$$C_g=C_1\left[1+\frac{\tan^2\delta}{1+z}\right]. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Thus the observed capacity is larger than the true capacity by an amount which depends on $z=\frac{C_0}{C_1}$ and $\tan\delta$. The larger the value of z—i.e., the more nearly the sample fills the air gap—the nearer does the observed value C_g approximate to the

true value C_1. If the sample is a poor insulator, then tan δ may be quite large. For a good conductor tan δ approaches an infinite value, and thus the method would give an infinite value for the capacity of such a material, although the true capacity might be quite small.

Now take the case of mercury electrodes, or rather the case in which metal electrodes of any sort are made to give as good a contact as possible with the dielectric, and the contact is then assumed to be perfect. Again the capacity is given by (7)—i.e., if C_m is the capacity given by this method

$$C_m=\frac{C_1C_0}{C_1+C_0}\left[1+\frac{C_0}{C_1}\cdot\frac{1}{1+\omega^2R_1^2(C_1+C_0)^2}\right]$$
$$=C_1\frac{\left[1+\frac{z}{1+(1+z)^2\cot^2\delta}\right]}{1+\frac{1}{z}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $z=\frac{C_0}{C_1}$ as before. In this case z is known to be very large—e.g., if the dielectric were 1 mm. thick, and there was an air film between electrode and dielectric equivalent to 0·001 mm. of dielectric—then we should have $z=1\,000$. Thus, as an approximation we may write

$$C_m=C_1\left[1-\frac{1}{z}\right]\left[1+\frac{z}{1+z^2\cot^2\delta}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Using the expressions (9) and (11), we may calculate the amounts by which the observed capacity, as measured by these two methods, will differ from the true capacity C_1. The results of such a calculation are given in the following table. The values taken for z are 9 for the air-gap method and 1,000 for the mercury electrode method.

TABLE I.—*Ratio of Observed Capacity to true Capacity.*

δ	tan δ	$\frac{C_m}{C_1}$	$\frac{C_g}{C_1}$
0° 35′	0·01	1—0·001	1·00001
5° 43′	0·1	1—0·001	1·001
17° 33′	0·316	1—0·0009	1·01
45° 0′	1·0	1·000	1·1
84° 18′	10·0	1·099	11·0
89° 26′	100·0	10·9	1001·0

We see that in every case the air-gap method gives the higher value of capacity. Thus high values of capacity obtained by the mercury method cannot be explained in this way. In the case of a good conductor the value of cot δ approaches zero, and thus the capacity observed by the mecury method approaches the value

$$C_1\left[1+\frac{1}{z}\right]^{-1}[1+z]$$

i.e., C_0, the contact capacity.

Consider now the power factor measurements. The quantity measured by a bridge method is the effective conductance—i.e., $\omega C_e \tan \delta_e$—where C_e is the effective capacity and $\tan \delta_e$ the effective value of the tangent of the loss angle. The value of the effective conductance in terms of what we have considered to be the true constants of the material is given by (5). Thus for the mercury method in the present case we have

$$C_m \tan \delta_m = C \frac{\omega k T}{1+\omega^2 T^2} = \frac{C_1 C_0}{C_1+C_0} \cdot \frac{\omega \cdot \frac{C_0}{C_1} R_1 (C_1+C_0)}{1+\omega^2 R_1^2 (C_1+C_0)^2}$$

$$= \frac{C_1}{1+\frac{1}{z}} \cdot \frac{z(1+z)\cot \delta}{1+(1+z)^2 \cot^2 \delta}$$

Since z is large compared with unity we may write this

$$C_m \tan \delta_m = \frac{C_1}{1+\frac{1}{z}} \cdot \frac{\tan \delta}{1+\left(\frac{\tan \delta}{z}\right)^2}$$

and by reference to (10) we see that this becomes

$$\tan \delta_m = \tan \delta \left[1+\left(\frac{\tan \delta}{z}\right)^2\right]^{-1} \left[1+\frac{z}{1+(1+z)^2 \cot^2 \delta}\right]^{-1} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

In the case of the air gap the test condenser is considered as consisting of two condensers in series, the sample, and the rest of the air gap. Thus the loss angle is calculated from the usual formula for condensers in series, which in the case considered becomes

$$\frac{C_0 \tan \delta_g}{C_0+C_g} = \frac{C_0 \tan \delta}{C_1+C_0}$$

$\tan \delta_g$ being the value obtained for $\tan \delta$ when using the air-gap method. Thus

$$\tan \delta_g = \tan \delta \cdot \frac{C_0+C_g}{C_0+C_1}$$

Substituting from (9) this becomes

$$\tan \delta_g = \tan \delta_1 \left[1+\frac{\tan^2 \delta}{(1+z)^2}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We may now use (12) and (13) to calculate the errors in $\tan \delta$ which may be expected in the different cases, exactly as was done for the capacity values. Table 2 gives the values for the cases (*a*) air gap where $z=9$, (*b*) mercury electrodes where $z=1\,000$.

TABLE II.—*Ratio of Observed and True Values of tan δ.*

δ	$\tan \delta$	$\frac{\tan \delta_m}{\tan \delta}$	$\frac{\tan \delta_g}{\tan \delta}$
0° 35′	0·01	$1-10^{-7}$	$1+10^{-6}$
5° 43′	0·1	$1-10^{-5}$	$1+10^{-4}$
45° 0′	1·0	0·999	1·01
84° 18′	10·0	0·909	2·0
89° 26′	100·0	0·090	101·0

Thus the errors only become considerable when the loss angle is very large, and in this case the result obtained with mercury electrodes is the more accurate. With very large power factors, the air-gap method will give too high a value, and the mercury electrode method too small a value. In practice the air-gap method would probably be unworkable with materials of high power factor, owing to want of uniformity of thickness and of perfect flatness in the specimen[17].

Barlow[15] maintains that owing to the high contact resistance it is useless to employ mercury electrodes in order to measure the true volume resistivity of dielectrics. This is probably true in the case of direct-current measurements, but the calculations here given show that when the current is alternating the observed value for the loss angle approximates closely to the true value, even when the contact resistance is infinitely great. In fact, if it is desired to measure the true resistivity of the material, measurements should be made at radio frequencies, for the effective conductivity at frequency $\omega/2\pi$ is given by

$$\sigma=\frac{Ck\omega^2T}{1+\omega^2T^2}$$

When the frequency is very high, so that ω^2T^2 is large compared with unity, this becomes

$$\sigma=\frac{Ck}{T}=\frac{C_1C_0}{C_1+C_0}\cdot\frac{C_0}{C_1}\cdot\frac{1}{R_1(C_1+C_0)}$$
$$=\frac{1}{R_1}\cdot\frac{1}{\left(1+\frac{1}{z}\right)^2}$$

And since z is large, this approximates to the true conductivity $\frac{1}{R_1}$. Consider Bairsto's[16] results for slate and marble. He found that as the frequency is raised the effective conductivity rises, rapidly at first, but afterwards more and more slowly, the value becoming approximately constant at the highest frequencies used (of the order 10^6 cycles per second). This value probably corresponds to the true resistivity of the material.

VIII. Conclusion.

It is not suggested that all the observed phenomena of absorption, dielectric hysteresis and power loss are due to these contact effects. In the case of substances which are not homogeneous in structure Maxwell's theory applies, and "after effect" phenomena would be observed whether these surface effects existed or not. In the case of quartz, iceland spar, etc., it is difficult to believe that heterogeneous structure provides an adequate explanation of the observed phenomena, and it is here that the present theory provides a more probable explanation. It is significant that there is a lack of agreement between the results of different observers on the decay of the absorption current with time. If this is largely a function of the electrode contact capacities and resistances, then the discrepancies are readily explained.

Another case in which this theory is of importance is that in which the dielectric is of comparatively poor quality—e.g., celluloid, glass and porcelain (especially at high temperatures), porous dielectrics, such as fabrics and paper, slate, and many

other insulators of importance commercially. In such cases it is quite probable that the insulator may better be regarded as a solid electrolyte, in which the ionic mobility is small, than as a true dielectric, and the effect of heterogeneous structure may be small compared with the contact effect. Many of the curious phenomena observed in such cases are easily explained by this theory. For example, the large positive temperature coefficient of the effective capacity of porcelain[17] is a direct consequence of the negative temperature coefficient of its resistance, for it is obvious from equation (7) that the smaller the value of R_1 the higher is the effective capacity.

The theory also suggests a possible explanation of the difference between the properties of solid and liquid dielectrics. Liquids do not show residual charge phenomena[5], and when they are subjected to an alternating voltage the power loss is practically independent of the frequency[20]. This may be due to the fact that in the case of a liquid (which wets the electrodes) the electrical contact is much more perfect, so that the contact resistance and capacity are no longer of importance. The power loss is simply due to the resistance of the dielectric, and is thus independent of the frequency. In this case the effective capacity is independent of the resistivity of the material, and the temperature coefficient of capacity is negative and not positive, as it is in the case where contact effects are large. Cassie[18] found that the temperature coefficient of capacity was positive for solids and negative for liquids.

A further interesting point which arises is the behaviour of the material under very high voltages. It seems probable that in this case the "contact capacity" would break down, so that the contact resistance would no longer be very great compared with the volume resistance. If this were so, then the "absorption current" would no longer be large compared with the leakage current. The behaviour of solid dielectrics under very high voltages has been studied by H. H. Poole[19]. He found that whereas at low voltages measurements of leakage resistance are very difficult owing to the absorption current being much larger than the leakage current, at high voltages this is not the case; but the absorption effect, if it then exists, is completely masked by the leakage current.

Thus there is a considerable amount of experimental work, for which the present theory provides an explanation. Quantitative comparisons are very difficult owing to the complexity of the results, but it is hoped in the near future to carry out an investigation on various dielectrics in order to see how far these considerations can be applied quantitatively.

List of References.

[1] Dye and Hartshorn. Proc. Phys. Soc., Vol. 37, p. 42, 1924.
[2] H. A. Wilson. Proc. Roy. Soc., Vol. 82, p. 409, 1909.
[3] Thornton. Proc. Phys. Soc., Vol. 22, p. 186, 1910.
[4] S. W. Richardson. Proc. Roy. Soc., Vol. 92, pp. 41, 101, 1916.
[5] Von Schweidler. Ann. der Physik., Vol. 24, p. 711, 1907.
[6] Curie. Annales de Chimie, 1889.
[7] Barlow. Jour. I.E.E., Vol. 62, p. 133, 1924.
[8] Addenbrooke. Jour. I.E.E., Vol. 57, p. 13, 1919. Proc. Phys. Soc., Vol. 27, p. 291, 1915.
[9] Richards. Physical Review, Vol. 22, p. 122, 1923.
[10] Meyer. Verh. Deutsch. Physik. Gesellschaft, Vol. 19, p. 139, 1917.

(11) Hopkinson. Collected Papers, Vol. I.
(12) Lubben. Archiv. fur Elektrotechnik, Vol. 10, p. 283, 1921. Von Schweidler. loc. cit.
(13) Wagner. Ann. der Physik, Vol. 40, p. 817, 1913.
(14) Wagner. Archiv. fur Elektrotechnik, Vol. 3, p. 67, 1914.
(15) Barlow. Jour. I.E.E., Vol. 62, p. 711, 1924.
(16) Bairsto. Proc. Roy. Soc., Vol. 96, p. 363, 1920.
(17) Haworth. Proc. Roy. Soc., Vol. 81, p. 221, 1908.
(18) Cassie. Phil. Trans. Roy. Soc., Vol. 181, p. 1, 1890.
(19) Poole. Phil. Mag., Vol. 32, p. 112, 1916; Phil. Mag., Vol. 34, p. 195, 1917; Phil. Mag., Vol. 42, p. 488, 1921.
(20) Pungs. Archiv. fur Elektrotechnik, Vol. 1, p. 329, 1912. Bryan. Physical Review, Vol. 22, p. 399, 1923.

DISCUSSION.

Prof. G. B. BRYAN asked whether the author's theory could explain the well-known experiment in which the metal coatings of a charged Leyden jar are found on removal to be themselves uncharged.

Mr. G. W. SUTTON: I have not yet had an opportunity of reading the Paper, but from Mr. Hartshorn's explanation of his theory it would seem that there should be a fairly simple and direct test of its validity. If there is a stratum of air imprisoned between the electrodes and the surface of the dielectric this air will become ionised and break down at a definite stress. If the D.C. voltage gradient is as he has represented it graphically on the board such a stress would probably be set up at some quite low voltage, and there should be some discontinuity in the voltage/displacement-current characteristic at fairly low values. It has been shown that some such effect as this does take place in the air-pockets which the process of manufacture is liable to enclose in the stratified dielectric of impregnated paper E.H.T. cables.

Mr. T. SMITH: According to the author's theory the properties of the dielectric are represented by the middle member of three shunted condensers placed in series. By suitable tests the constants of this condenser and the associated resistance can be determined, and observations of this kind can be made for a series of slabs of the same material of different thicknesses. A test of the acceptability of the theory may be obtained by ascertaining whether the changes in these constants for the several pieces of material are in accord with the differences in their dimensions. Has the author been able to justify his theory by such a series of experiments?

AUTHOR'S reply: In reply to Prof. Bryan, I think that absorption plays but a very small part in the old Leyden jar experiment. Mr. Addenbrooke (Phil. Mag., Vol. 43, p. 489, 1922) has shown that when the Leyden jar has paraffin wax as dielectric, the metal coatings, on removal, are found to possess large charges, and if they are discharged and the jar re-assembled, the whole arrangement possesses very little charge. This small charge is probably due to absorption, and can be explained by the theory I have proposed. The well-known historical experiment only succeeds when glass is used as dielectric, and even in this case the glass must not be perfectly dry. In fact, the explanation seems to be that the real electrodes of the jar are not the metal coatings, but films of moisture on the glass. The metal coatings merely serve as convenient terminals, the removal of which in no way affects the charges on the actual electrodes, the moisture films. I should not expect the action described by Mr. Sutton to occur to any marked extent in the case of ordinary dielectrics, although such actions do appear to explain the ionisation points of certain cables. Fig. 1 of the Paper is only diagrammatic, and the high resistance property of the contact surface is not necessarily due to air. There is certainly discontinuity in the electrical properties at the contact surface, and I have imagined this to have the effect of a very high contact resistance, but the physical nature of this is by no means obvious. An air film would of course possess a high resistance at low voltages, and would break down at high voltages, but the order of the breakdown voltage of films one or two molecules thick is rather an unknown quantity. It is not likely that the ordinary process of ionisation by collision would occur. On the whole an air film does not seem to supply an adequate explanation. I have had under consideration for some time a series of experiments like those outlined by Mr. T. Smith, since they are obviously of fundamental importance, but owing to pressure of other work I have not yet any results to communicate.

XX.—A MAGNETIC BRIDGE FOR TESTING STRAIGHT SPECIMENS AND AN ANALYSIS OF THE HYSTERESIS LOOP OF COBALT-CHROME STEEL.

By Edward Hughes, *B.Sc.*, *A.M.I.E.E.*

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(*Communicated by* Wm. Bennett, *B.Sc.*)

Abstract.

The author employs a permeameter resembling that of Iliovici, in which the currents in two coils providing the M.M.F. of a magnetic circuit containing the specimen are adjusted until no magnetic potential difference exists between a selected pair of fixed points on the specimen. In the present apparatus the required absence of magnetic potential difference is tested by bringing up a yoke till its ends abut upon the two points in question: the approach of the yoke should excite no current in a search coil wound on the specimen and connected in a low-resistance galvanometer circuit. Resistance is then added to the galvanometer, and the deflection caused by a reversal of the two magnetizing currents enables the flux density to be calculated. The hysteresis loss per c.c. per cycle in cobalt-chrome steel is found by this method to be approximately $0{\cdot}056\,B_{max.}^{1{\cdot}7}$ ergs, though the index of $B_{max.}$ actually decreases with increasing values of the flux density. The magnetization curve for this substance, above the point of inflexion near the origin, is found to be given by $\frac{H-c}{\beta}=d+\frac{H}{\beta_s}$, where $\beta=B-H$, β_s is the saturation value of β, and c, d are constants. To form a permanent magnet whose external energy per c.c. is within 5 per cent. of the maximum obtainable, a magnetizing force of upwards of 1,000 C.G.S. units must be applied to cobalt-chrome steel. The βH loop between the $+\beta$ and $-H$ axes is given by a formula similar to that for the magnetization curve, with different constants instead of c, d, β_s, the value corresponding to β_s being much less than the true saturation density.

MANY forms of permeameters* have been devised for testing bars of magnetic material, but most of them involve careful machining to reduce the reluctance of the joints, and require yokes of very low reluctance compared with that of the specimen under test; and the few permeameters that can be used to determine the hysteresis loop with accuracy are complicated and cumbersome. The magnetic bridge described in this Paper is of simple construction, and enables both the magnetization curve and the hysteresis loop of a bar to be obtained accurately over a wide range of magnetizing force.

Let us first consider a permeameter due to Iliovici, to which the writer's apparatus bears much similarity in that the M.M.F.s of two coils, acting on a common magnetic circuit, are so related that there is no magnetic potential between two particular points of that circuit. Thus, in Fig. 1, AB represents the bar to be tested, having a magnetizing coil NN and a search-coil S; and CD is a yoke carrying a winding M. An auxiliary yoke Y with search-coil T, is clamped firmly against AB.

After the specimen is demagnetized, switch V is put over to T; and with a given current through N, that through M is varied until a reversal of the exciting currents does not give a deflection on the galvanometer scale. V is then changed over to S, and the galvanometer deflection is noted for a reversal of the magnetizing

* *See* Dictionary of Applied Physics, Vol. II., pp. 474-486.

currents. The flux density in AB for a given M.M.F. between the points of contact of Y with AB can then be determined. Such a method eliminates the reluctance of the joints from the calculation but it possesses the following disadvantages :—

(1) The portions CD and AB of the magnetic circuit generally have different time-constants, with the result that the flux in one part grows more rapidly than that in the other ; consequently the galvanometer may give a double kick, moving

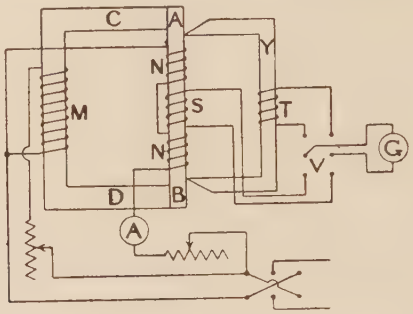

Fig. 1.

first in one direction and then in the opposite direction. Under such circumstances, it is impossible to obtain an exact magnetic balance.

(2) Since coil N has to be made of appreciable magnitude in order to obtain a magnetizing force up to, say, 400 or 600, it is impossible to avoid a certain amount of leakage flux passing through the search-coil on Y, even though there be no magnetic potential between the points of contact of Y and AB.

(3) The apparatus cannot be used to determine the hysteresis loop, since the relationship between the permeabilities of AB and CD is not constant.

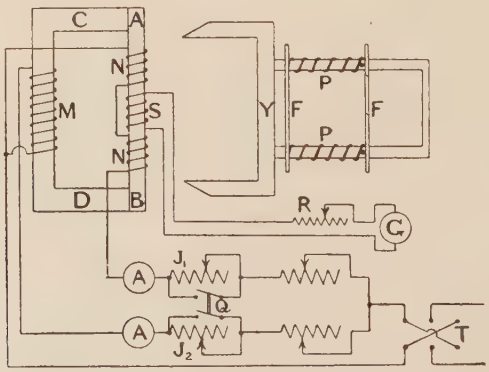

Fig. 2.

These disadvantages have been overcome by arranging yoke Y to be carried by two rods passing through guide-plates FF, with light springs PP to draw Y away from AB (Fig. 2). Coil NN is fixed to the base of the instrument, and made with sufficient clearance inside to allow easy replacement of AB by other samples. Search-coil S is wound directly on to the specimen under test. With a bar $\frac{3}{4}$ in. by

$\frac{3}{16}$ in. in section, and with 200 turns on S, 6,000 ohms were required in the galvanometer circuit to limit the deflection to a reasonable value when the maximum flux was being reversed. The resistance of the galvanometer and coil S was only 11 ohms; so that with R reduced to zero, the galvanometer was very sensitive to change of flux through S.

Fig. 2 also shows the circuit arrangement for taking a hysteresis loop, the test procedure being as follows :—

With the D.P. switch Q closed and the maximum magnetizing current through NN, the current through M is adjusted until on moving Y up to AB, there is no

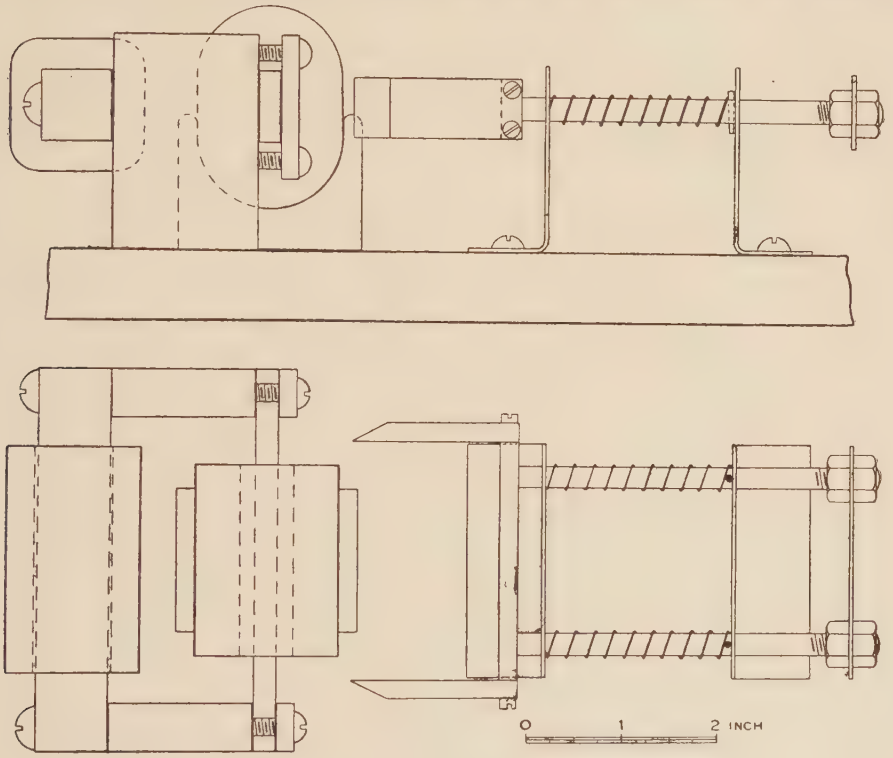

Fig. 3.

galvanometer deflection with R at zero. There is no difficulty in detecting an alteration of 1 per cent. of the current through M. It is, of course, essential to reverse the exciting currents several times after each adjustment, so as to ensure the magnetic circuit being in a steady cyclic condition. If the movement of Y up to AB or away from AB causes no change of flux through S, it follows that the points of contact of Y and AB are at the same magnetic potential. After the adjustment has been made, a suitable resistance is inserted into the galvanometer circuit, and the deflection is noted for a reversal of the exciting currents.

Switch Q is next opened, and J_1 is adjusted to give another value of the current. Q is closed, T is reversed several times, and then Q is opened and T reversed simultaneously. The magnetic balance is tested by moving Y towards AB, and J_2 is

adjusted to give a balance. As this adjustment may have caused a departure from the correct loop, it is necessary to repeat the test. Usually two or three repetitions enable the correct balance to be obtained.

The test is repeated with different values of J_1 up to infinity, and then with decreasing values but without reversing T.

The apparatus made at the Technical College, Brighton, was designed to test bar magnets 4 in. by $\frac{3}{4}$ in. by $\frac{3}{16}$ in., and is shown in Fig. 3, the windings being as follows :—

Coil NN =168 turns of No. 18 S.W.G.
,, M =150 ,, No. 18 ,,
,, S =200 ,, No. 36 ,,

Coil NN was wound in six layers with tappings between the second and third

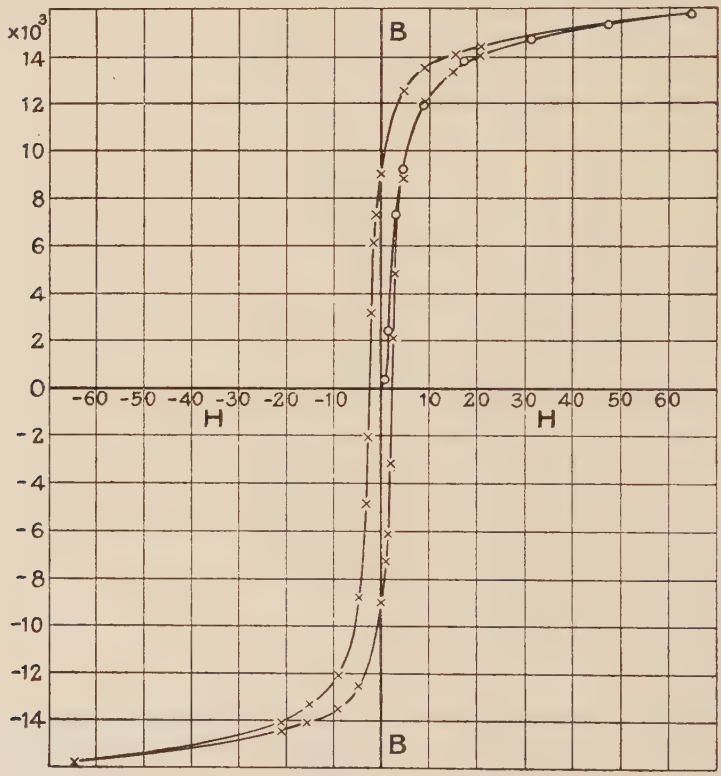

Fig. 4.

and between the fourth and fifth. The three sections were tested separately with the same current, but there was no measurable difference in the magnetic balance nor in the galvanometer deflection. Also the flux through S was measured (a) with yoke Y away from AB and (b) with Y pressed against AB, but again there was no measurable difference. With the windings immersed in oil, there was no difficulty in working up to a magnetizing force of 600.

In order to test the behaviour of the apparatus with materials of widely different magnetic characteristics, bars of mild steel and of cobalt-chrome steel were used. The circles and crosses in Fig. 4 indicate the points for the magnetization curve and for the hysteresis loop respectively of the mild-steel bar. It is seen that there is no difficulty in obtaining consistent results on the steep portion of the loop even with very low coercive force. It may be of interest to note how closely the magnetization curve of this specimen agrees with the well-known expression of Kennelly* :—

$$\rho_0 = \frac{H}{\beta} = a + \frac{H}{\beta_s},$$

where ρ_0=ferro-magnetic or metallic reluctivity,

β=ferro-magnetic density for a magnetizing force H,

$=B-H$,

β_s=ferro-magnetic saturation density,

and a=a constant.

The values of ρ_0 have been plotted in Fig. 5 for H up to 224 c.g.s.units, the values

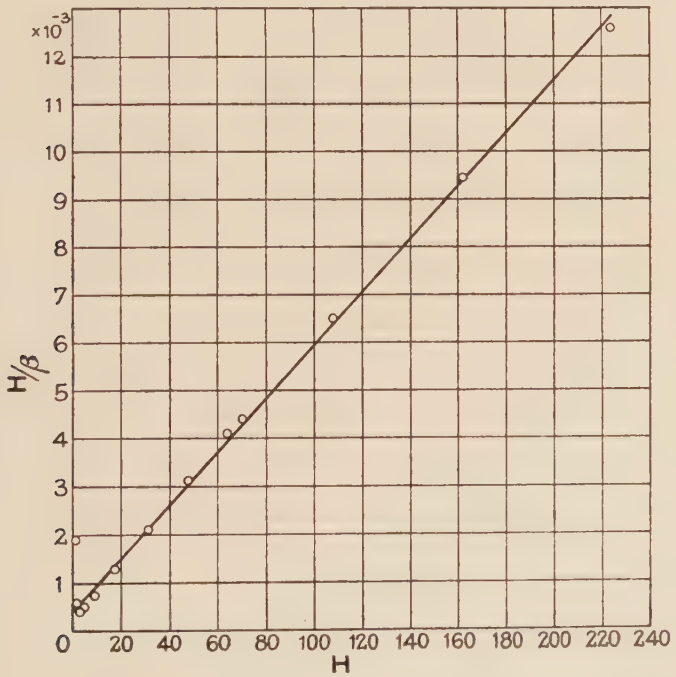

Fig. 5.

* A. E. Kennelly, "Magnetic Reluctance," Trans. Amer. I.E.E., Vol. 8, p. 485 (1891).

of β_s and a for the line drawn through the mean* of the points being 18,000 and 0·00042 respectively.

Three different qualities of cobalt-chrome steel supplied by the Cobalt Magnet Steel Co., Sheffield, were also tested. Table I gives the composition of these specimens, and Fig. 6, obtained on specimen *B*, is representative of the magnetization curve and hysteresis loops of the three samples.

TABLE I.

Specimen.	C	Cr	Co	Mo	W	Mn
A	1·0	9·72	15·0	1·42	...	...
B	1·0	9·72	9·0	1·42	...	...
C	0·9	5·6	36·0	...	4·0	0·9

The values of the coercive force, the remanence and the energy represented by the different loops taken on the three specimens are given in Table II. Data supplied by the manufacturers showed specimens *B* and *C* to be of the average quality and *A* to be a little inferior to the average specimen of that composition.

TABLE II.

Specimen.	$B_{max.}$	Coercive force.	Remanence.	Ergs/c.c./cycle.
A	12,300	190	7,600	$50{\cdot}9\times10^4$
	10,830	181	7,120	$44{\cdot}35\times10^4$
	8,950	156	5,780	$32{\cdot}1\times10^4$
	6,840	127	3,960	$19{\cdot}22\times10^4$
	4,650	86	2,080	$8{\cdot}535\times10^4$
B	12,520	160	7,870	$46{\cdot}1\times10^4$
	11,030	156	7,470	$40{\cdot}45\times10^4$
	9,700	145	6,530	$33{\cdot}2\times10^4$
	6,800	109	4,040	$16{\cdot}85\times10^4$
	3,910	70	1,660	$5{\cdot}51\times10^4$
C	14,740	210	9,620	$68{\cdot}5\times10^4$
	13,160	200	8,850	$59{\cdot}65\times10^4$
	10,450	177	6,750	$40{\cdot}9\times10^4$
	6,950	129	3,620	$18{\cdot}78\times10^4$
	4,110	64	1,235	$5{\cdot}43\times10^4$

The hysteresis loss per c.c. per cycle can be represented approximately by:—

$$W=kB^x_{max.}$$

so that $\log W=\log k+x\log B_{max.}$

In the lower portion of Fig. 7, $\log W$ has been plotted against $\log B_{max.}$ for each

* The variation in the slope of the reluctivity curve has been discussed by C. P. Steinmetz in the General Electric Review, Vol. 20, p. 135, 1917, and by W. L. Cheney in Scientific Papers, Nos. 361 and 404, of the Bureau of Standards.

of the three specimens, and the values of x for different flux densities are given by the upper set of curves. If 1·7 be taken as the mean value of x for the three specimens, the hysteresis loss can be represented fairly closely by

$$\text{Hysteresis loss/c.c./cycle} = 0{\cdot}056\ B_{\text{max}}^{1{\cdot}7}.\ \text{ergs.}$$

It is of interest to note that the index of B for cobalt-chrome steel decreases

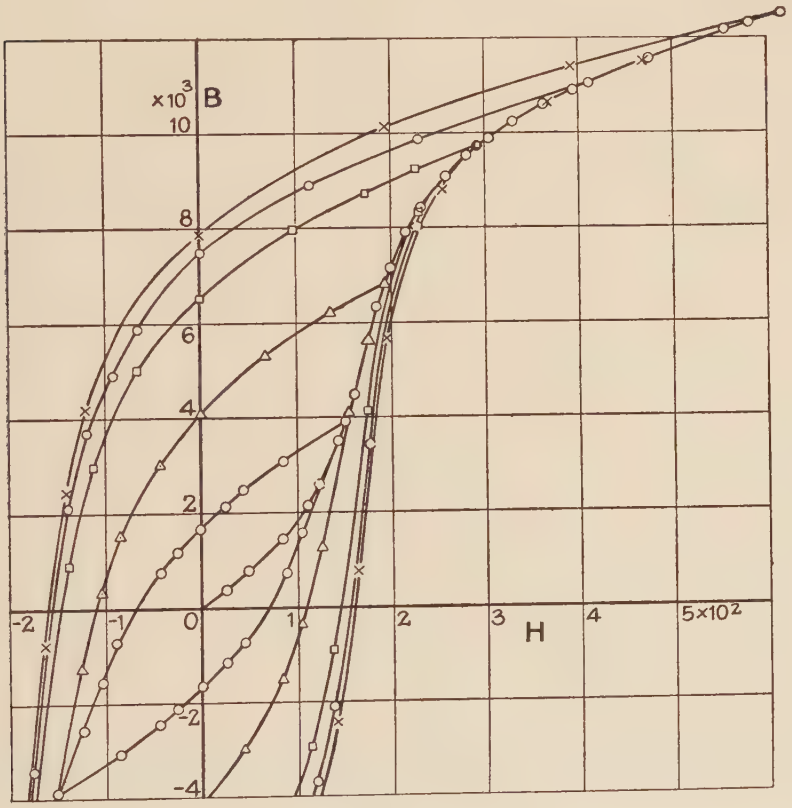

Fig. 6.

with increase of B, whereas for soft-iron and silicon-steel alloys, the reverse effect* has been found by various investigators.

Expression for the Magnetisation Curve of Cobalt-Chrome Steel.

The expression for H/β given on page 237 represents very closely the magnetization curve of homogeneous magnetic materials having narrow hysteresis loops and therefore only a small point of inflexion near the origin. When applied to

* E. Hughes, "Iron Losses in D.C. Machines," Journal I.E.E., Vol. 63, p. 39 (1924).

cobalt-chrome steels, however, the above expression requires some modification.* If the magnetization curve forms a part of a hyperbola on *PQ* and *PR*

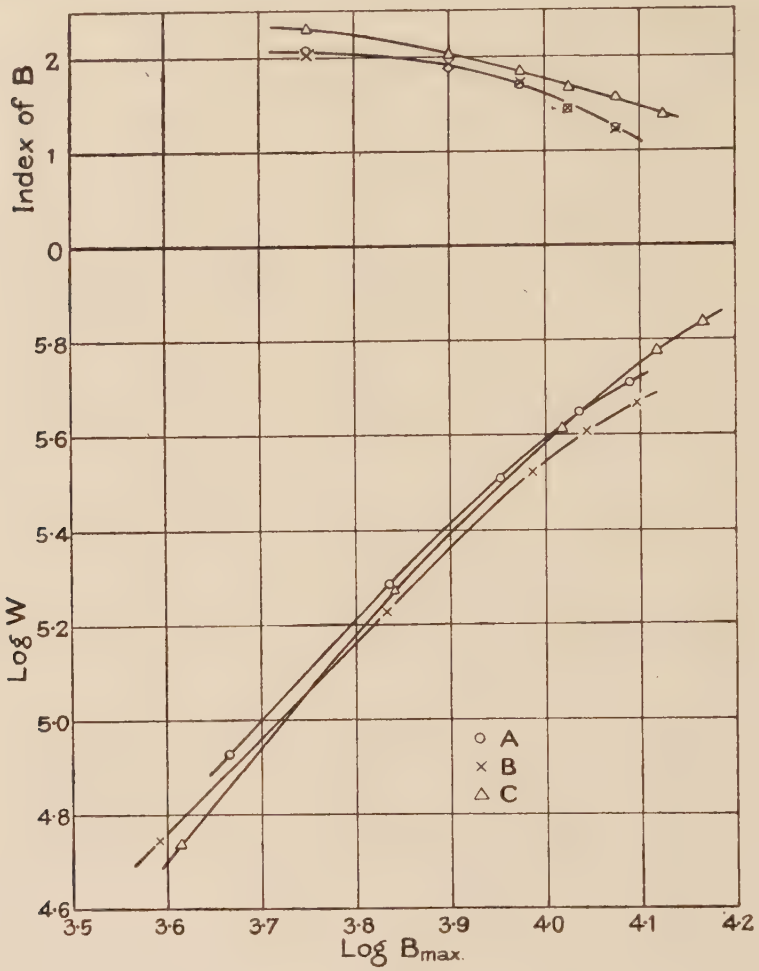

FIG. 7.

* Curves of H/β for different qualities of steel tested up to very high flux densities are given in the following Scientific Papers of the Bureau of Standards ; but a much greater portion of the magnetization curve determined for each of the cobalt-chrome specimens is in agreement with expression (*a*) derived below than with Kennelly's expression.

(1) W. L. Cheney, " Magnetic Testing of Straight Rods in Intense Fields," No. 361, p.625, Vol. 15 (1920).

(2) Sanford and Cheney, " Variation of Residual Induction and Coercive Force with Magnetizing Force," No. 384, p. 291, Vol. 16 (1920).

(3) Nusbaum, Cheney and Scott, " Magnetic Reluctivity Relationship as related to certain Structures of a Eutectoid-Carbon Steel," No. 404, p. 739, Vol. 16 (1920).

as axes (Fig. 8), then β_s represents the ferro-magnetic saturation density and we have

$$(\beta_s-\beta)(H-a) = \text{a constant}$$
$$= m \text{ (say)}$$
$$\text{When } \beta=O,\ H=c$$
$$\therefore\ m=b(c-a)$$

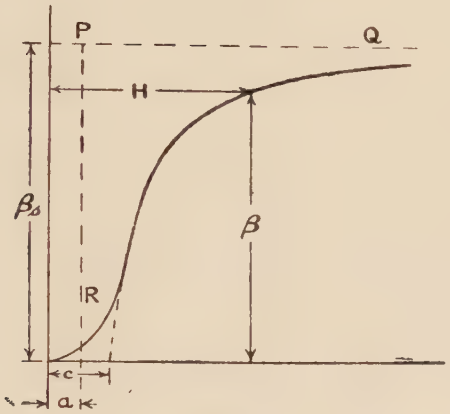

FIG. 8.

Substituting for m and simplifying, we have

$$\frac{H-c}{\beta}=-\frac{a}{\beta_s}+\frac{H}{\beta_s}$$
$$=d+\frac{H}{\beta_s} \quad \ldots\ldots\ldots\ldots\ (a)$$

where $d=-\frac{a}{\beta_s}$=a constant for a given specimen.

From the magnetization curves for the three specimens of cobalt-chrome steel the following values have been derived :—

TABLE III.

Specimen.	β_s	c	d
A	13,700	140	—0·00403
B	14,200	100	0
C	15,800	185	—0·00826

Fig. 9 has been plotted with $\frac{H-c}{\beta}$ against H, and the curves show that apart from the initial portion, the magnetization curve follows the hyperbolic law very closely for the range of magnetizing force covered by these experiments.

VARIATION OF $(\beta/H)_{max.}$ WITH $H_{max.}$ AND $\beta_{max.}$.

It is now well known that one of the most important characteristics of a permanent magnet is the maximum value of the product of β and H for

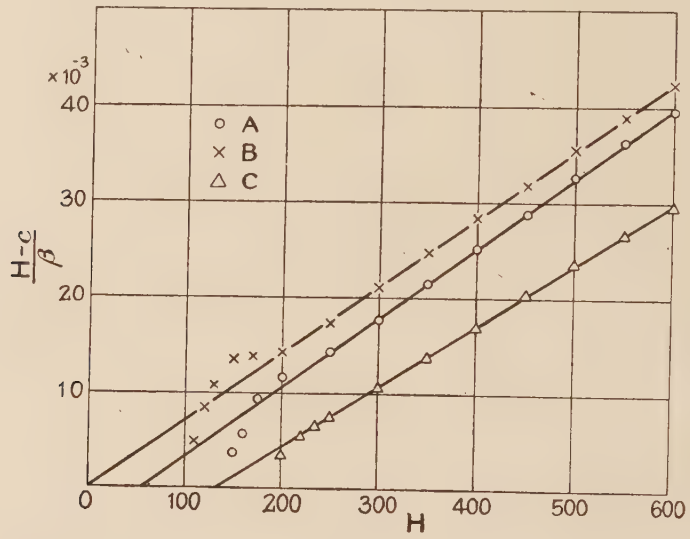

FIG. 9.

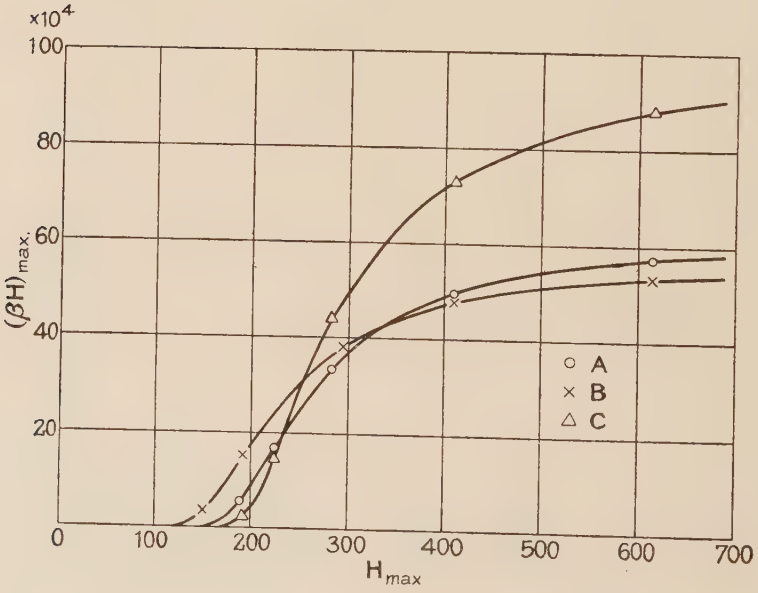

FIG. 10.

that part of the hysteresis loop lying between the $+\beta$ and the $-H$ axes. Thus, Evershed* has shown that the external energy maintained by 1 c.c.

* "Permanent Magnets in Theory and Practice," Journal I.E.E., Vol. 58, p. 798 (1920).

of magnet steel at flux density β is $\frac{\beta H}{8\pi}$ ergs. The dependence of $(\beta H)_{\text{max.}}$ upon the maximum value of the magnetizing force is seen from Fig. 10, the values being derived from the respective curves of the three specimens of cobalt-chrome steel. It is impossible to extrapolate sufficiently accurately to obtain the maximum value of $(\beta H)_{\text{max}}$ for a given specimen. Consequently Fig. 11 has been drawn with $(\beta H)_{\text{max.}}$ plotted against the value of $\beta_{\text{max.}}$ for the corresponding loop, and the curves are produced to the saturation values of β already given in Table III. Comparison of Figs. 10 and 11 shows that to obtain values of $(\beta H)_{\text{max.}}$ within 5 per

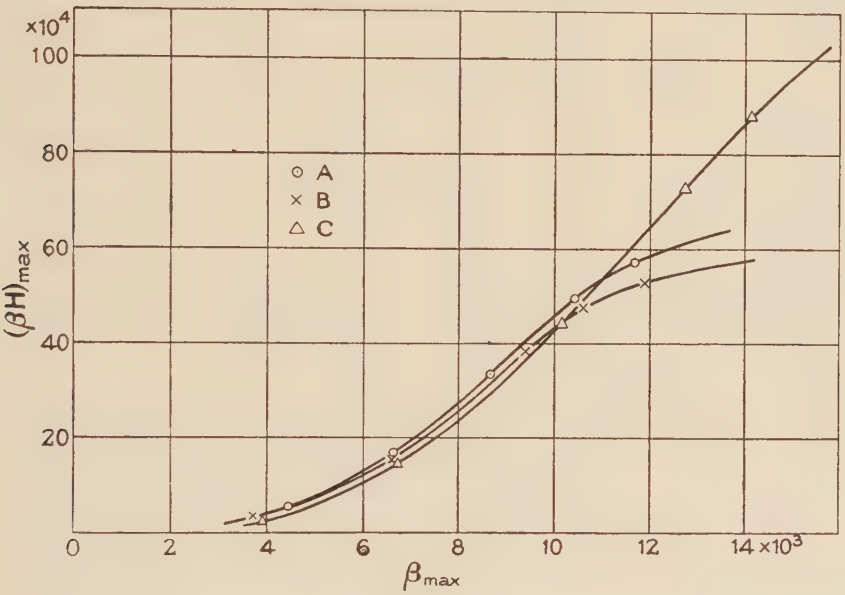

Fig. 11.

cent. of the maximum possible, it is necessary to apply a magnetizing force of at least 1,000 c.g.s. units—preferably about 1,500 or 2,000 units.

From Fig. 11 the following table has been derived :—

Table IV.

Specimen.	Maximum Value of $(\beta H)_{\text{max.}}$	Maximum External Energy per c.c. of Magnet.
A	64×10^4	$2{\cdot}55 \times 10^4$ ergs
B	58×10^4	$2{\cdot}31 \times 10^4$ ergs
C	103×10^4	$4{\cdot}1 \times 10^4$ ergs

It has been pointed out by E. A. Watson* that the portion of the βH loop

* " Permanent Magnets, and the Relation of their Properties to the Constitution of Magnet Steels," Journal I.E.E., Vol. 61, p. 644 (1923).

lying between the $+\beta$ and the $-H$ axes is approximately hyperbolic in shape. It can, therefore, be represented by an expression of the form

$$\frac{H-c'}{\beta}=d'+\frac{H}{\beta'_s} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (b)$$

where c'=value of H at which the βH curve cuts the H axis.

$\doteqdot$coercive force,

β'_s=*apparent* saturation density,

and d'=a constant.

The values of c', etc., that give the closest agreement between the above ex-

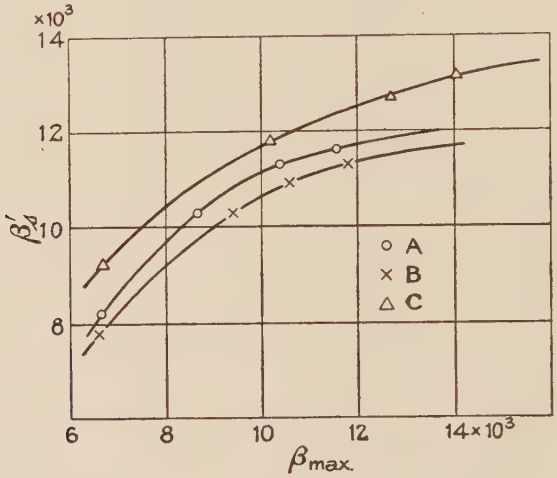

FIG. 12.

pression and the actual curve between the limits $H=O$, $\beta=\beta_{rem.}$ and $H=c'$, $\beta=O$, are tabulated below :—

TABLE V.

Specimen.	c'	d'	β'_s	Maximum Value of β'_s from Fig. 12.
A	—190	0·025	11,600	12,000
B	—160	0·0203	11,300	11,700
C	—210	0·0218	13,150	13,400

A comparison of the values of β_s and β'_s in Tables III. and V. respectively shows that the saturation density derived from expression (b) is in each case much smaller than the true value given by (a) p. 241, so that the true saturation density of the magnet can not be used to construct that portion of the βH loop that lies between the $+\beta$ and the $-H$ axes.

It may be argued that the values given for β'_s in Table V are not comparable with those for β_s, in Table III, owing to the maximum value of the magnetizing force being only 615. In order to check this argument, the values of β'_s for the

different hysteresis loops have been determined, the results being plotted against the maximum values of β for the respective loops. The curves (Fig. 12) have been produced to the saturation densities given in Table III, and the corresponding values of β'_s have been determined and inserted in Table V. They are, however, much smaller than the true values of the saturation density.

Conclusions.

(1) The magnetization curve and the hysteresis loop of magnetic bars of widely different qualities can be determined easily and accurately by means of the magnetic bridge described above.

(2) The hysteresis loss in cobalt-chrome steel is given fairly closely by

$$\text{Hysteresis loss/c.c./cycle} = 0{\cdot}056\, B_{\text{max.}}^{1{\cdot}7} \text{ ergs.}$$

(3) The magnetization curve of cobalt-chrome steel—apart from the point of inflexion near the origin—is hyperbolic and can be represented by an expression

$$\frac{H-c}{\beta} = d + \frac{H}{\beta_s}$$

(4) The maximum value of the external energy maintained per c.c. of magnet depends greatly upon the maximum value of the magnetizing force applied to the magnet ; and to obtain values within 5 per cent. of the maximum possible, a magnetizing force of at least 1,000 units—preferably 1,500 to 2,000 units—must be applied.

(5) The portion of the βH loop between the $+\beta$ and the $-H$ axes is approximately hyperbolic, but the value of β'_s for this portion is much less than the true saturation density β_s of the material. It is, therefore, not correct to utilise the value of β_s when constructing graphically this part of the βH loop of a magnet, nor to term β'_s the saturation density of the material.

DISCUSSION.

Mr. D. W. Dye : The modification of the means of ascertaining that the compensation for reluctance of the joints, etc., of the Iliovici permeameter has been correctly made appears to be a considerable improvement in this apparatus. The use of a movable exploring yoke instead of the reversal of the main magnetizing current is in effect equivalent to the introduction of a statical means of determining that the magnetic potential difference between the two points of contact of Y with the specimen is sensibly zero. The straightness of the reluctivity curves shows that this method of indication is not seriously in error when magnetizing forces greater than about 5 C.G.S. units are in operation. Since, however, the causes mentioned under (2) on page 234 are still operating when the yoke is brought up into contact with the specimen, the condition experimentally realised is actually that the magnetic potential difference between the points of contact of the specimen remains unaltered when the yoke is brought into contact and not necessarily that this magnetic potential difference is quite zero. There will, in general, be a small magnetic potential difference between the ends of Y owing to the leakage field referred to. The effect on the curves obtained by the apparatus will be to shear the hysteresis loop in such a fashion that the coercive force points remain unaltered. This effect still leaves the loop of a normal looking shape and no immediate judgment can be made as to its accuracy. It is when such loops are obtained by a more standard method that the differences are observed ; it is doubtful whether the hysteresis loops of materials having a coercive force of 2 C.G.S. units or less can be accurately measured by any type of permeameter in which H is deduced from a magnetizing current and an effective length of specimen which is determined or adjusted to a known value experimentally. The conditions are, of course, very different in the case of materials in the other extreme condition, i.e., hardened magnet steels. An uncertainty in H of 1 unit at the remanence point is of comparatively little importance.

With regard to the statement that the Iliovici permeameter cannot be used in its normal form for hysteresis loop determinations, I am not quite clear why this should be so. If the procedure outlined by the author when using his method is followed except that the search coil T is used, then by whatever means the M.M.F. is provided round the path $A\ C\ M\ D\ B$ of Fig. 1, so long as the final result at the test points of Y is a sensibly zero magnetic potential difference, then the M.M.F. provided by N is that which is expended along the specimen up to the two test points of the yoke Y. The switching procedure by which the desired point on the loop is reached must, of course, be exactly rehearsed when testing by search coil T. The advantages of the movable yoke are, however, so obvious that the point need not be pressed further.

The chief cause of the double throw referred to by the author is, I think, the solidity of the main yoke. In testing apparatus used at the National Physical Laboratory, in which yokes of large section are used, we have found it very advantageous to build them up of laminations of stalloy sheet punched to a suitable shape.

The observations on the variation of the hysteresis index as a function of $B_{max.}$ are of considerable interest. There is a field for much investigation on this point. The variations of the index appear to be associated with curvature of the BH curve. In the case of the softer magnetic materials, there seems considerable ground for believing that the index rises as B diminishes from a value near to 2,000 to zero, and that it rises again from 12,000 upwards. At values of B above 17,000 or 18,000 it is to be anticipated that the index must fall again since the hysteresis loop is tending to a finite area, although $B_{max.}$ may continually increase.

The introduction of the additional constant "c" in the reluctivity equation (a) is an improvement not only in that it enables a greater portion of the βH curve to be represented, but also in that it suggests a line for future work in correlating "c" with the coercive force of the material. this also follows from the experimental fact that the portion of the hysteresis loop between $\beta_{rem.}$ and $+H_c$ follows very closely the βH curve. We have found this to hold for many kinds of magnetic material. With regard to the author's conclusion as to the high magnetizing force required if the maximum energy per c.c. is to be retained, I have found this to be true for cobalt steels, but for ordinary tungsten magnet steels it is unnecessary to carry the magnetizing force to such high values. A good rule to adopt in tests on magnet steels of all kinds is to carry the magnetizing force up to a value of 8 or 10 times the coercive force expected.

Dr. D. Owen suggested that some of the difficulties of Iliovici's method might have been got over by the use of a fluxmeter, but the present method shares with the magnetometer method the advantage that it enables time changes to be observed by applying the test yoke a second time after an interval of fifteen seconds or so. Had the author examined in this way the question whether a balance when once obtained was permanent for a given adjustment? Similarly, it would be possible to observe the effect of a rise in temperature. No physical explanation was available for the usual increase of the index of B, in Steinmetz' formula, with increase in the value of B. The author's discovery that in the case of cobalt-chrome steel the index decreases instead of increasing adds another phenomenon to those which must be explained by any theory on this subject.

Mr. Rollo Appleyard referred to the fact that in Iliovici's original method two successive kicks of the galvanometer are obtained for each reversal of current, as mentioned by the author. Is this phenomenon to be attributed to the difference in the lengths of the two magnetic paths concerned? How are the time constants relevant to the respective kicks to be defined?

Mr. W. C. S. Phillips asked how long it takes to carry out a test by this method? It used to be usual to specify the coercive force and retentivity of magnets, but it was difficult to get rapid determinations for commercial purposes. Had the author checked his results against standard determinations, and what limits of accuracy did he attribute to his method?

Author's reply (communicated): Mr. Dye has drawn attention to the effect of leakage flux in the movable yoke Y, and further tests have been made to check the magnitude and distribution of this flux. Six search coils were wound in positions indicated in Fig. A. The bridge was balanced in the usual manner, and galvonometer deflections were noted for the six search coils in turn, when

(a) The exciting currents were reversed with Y at its maximum distance from the core;
(b) Ditto with Y pressed against the core;
(c) Y was moved up to the core, the exciting currents not being reversed.

The M.M.F. of coil NN was 1060, and the flux density in AB (Fig. 2) was 8140. The cor-

responding fluxes in coils 1 to 6 in test (*a*) were 160, 158, 152, 126, 96 and 63 respectively. In test (*b*) it was found practically impossible to obtain reliable figures owing to the double-kick effect referred to in the Paper. Test (*c*) indicated a change of flux of 47, 47, 43, 31, 16 and 39 in coils 1 to 6 respectively. A very definite double-kick was obtained with coil 6, indicating first an increase and then a sudden decrease of flux as *Y* was moved up to the core. The difference between the fluxes in tests (*a*) and (*c*) gives the flux when *Y* is held against the core, the flux densities thus calculated for positions 1 to 6 being 141, 139, 136, 119, 10) and 30 respectively, an average of, say, 110 for the whole length of *Y*. The permeability of the yoke at these low flux densities is not known ; but assuming a value of, say, 200, we find that the magnetic potential drop along the whole of *Y* is $\frac{110 \times 14{\cdot}5}{200}$, namely, 7·97. This figure indicates a possible error of 0·75 per cent. in the value of the M.M.F. acting between the two test-points of specimen *AB*. Similar tests carried out for other values of the exciting currents confirmed the above conclusion, and also indicated that the leakage flux in *Y* with the bridge balanced was practically proportional to the exciting M.M.F.

Another method of checking the effect of the leakage flux through *Y* was carried out thus : The bridge was balanced in the usual manner and the current in *M* (Fig. 2) noted. Yoke *Y* was then held against the core, and the current through *M* readjusted until the net deflection—i.e.,

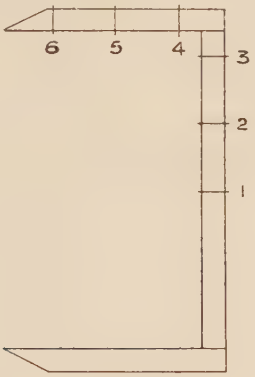

Fig. A.

the double-kick—in search-coil (1) was as nearly as possible zero. The fluxes in coils (5) and (6) were then found to be in the reverse direction to that when the bridge was balanced by the first method, indicating that the magnetic potential drop in *Y* had been reversed. The currents in *M* for the two methods of balancing were 1·93 and 1·91 respectively, so that the error involved in either method is well under 1 per cent. The M.M.F. due to coil *NN* was maintained constant at 1060.

I do not see why this type of apparatus is not suitable for testing materials having a coercive force less than 2 C.G.S. units, as suggested by Mr. Dye. It has already been stated that the leakage flux in *Y* appears to be roughly proportional to the exciting M.M.F., so that any error due to that cause should be approximately constant. On the other hand, the elimination of the reluctance of the joints would seem to make this type of apparatus particularly suitable for such work. Further, the yoke—being movable—has its residual flux (if any) reduced to the minimum before it is moved up to the specimen under test. This is a decided advantage over the fixed yoke when very low magnetizing forces are being dealt with.

Mr. Dye is correct in stating that the Iliovici permeameter can be used—theoretically—for determining the hysteresis loop ; but the double-kick effect renders it practically impossible with a ballistic galvanometer, though this difficulty could be overcome by the use of a fluxmeter, as suggested by Dr. Owen.

I am interested in Mr. Dye's suggestion that the variation in the hysteresis index may be associated with the shape of the *BH* curve. It seems difficult to anticipate the behaviour of the index at very high values of the maximum magnetizing force. Both $B_{rem.}$ and H_c have been

shown by Sandford and Cheney (p. 240) to be functions of the maximum magnetizing force; so that though the area of the hysteresis loop with magnetizing forces of a high order may be increasing very slowly, the value of $B_{max.}$ will be increasing more slowly. It does not seem, therefore, that the hysteresis index must necessarily decrease.

Mr. Dye's suggestion of a possible relationship between the coercive force and the constant "c" may also lead to useful results. It may be added that since submitting the Paper, equation (1) has been applied to data given in the Papers of the Bureau of Standards referred to on p. 238. For the samples of Honda magnet steel, it was found that the graph based on this equation indicated in each case a definite alteration of slope at a magnetizing force of about 750—a feature that was veiled by the curvature of the ordinary reluctivity graph. The whole of the data in the Paper, with the exception of Figs. 4 and 5, refer to cobalt-chrome steel; and the high magnetizing force of over 1000 is not meant to apply to other materials.

In reply to Dr. Owen, it may be stated that no effects of time or temperature were noticed. In all the tests the exciting currents were reversed a number of times before taking a reading, and such readings were found to be perfectly consistent and independent of time. For most of the tests the apparatus was immersed in oil, so that the temperature rise of the specimen was very small. When mild steel was being tested at a low magnetizing force, it was found that its flux was disturbed by a sharp impact of Y against the specimen.

Mr. Dye has dealt with the question of the double-kick phenomena raised by Mr. Appleyard. The term "time-constant" refers to the growth of flux in the magnetic circuit concerned, and not to the duration of a kick. It can therefore be defined in the orthodox manner.

With regard to the time taken to determine a single loop, a set of, say, 10 points with three galvanometer readings per point can be taken in about 30 minutes. The remanence itself can be obtained very quickly; but for finding the coercive force the simplest procedure is to take readings for two or three points in the neighbourhood of zero flux. It may be mentioned that other methods* are available for quick determination of the portion of the hysteresis loop lying between the $+B$ and the $-H$ axes.

No other reliable permeameter was available for testing straight specimens, so that it is not possible to state the limits of accuracy of the present apparatus. It is estimated, however, from a consideration of possible errors, that the net error should not exceed about 1 per cent.

* Dictionary of Applied Physics, Vol. II, p. 493; and Journal I.E.E., Vol. 61, p. 659 (1923).

XXI.—THE EXPERIMENTAL CONTROL OF ELECTRICALLY BROADENED SPECTRAL LINES.

By M. C. Johnson, *B.A.*

Received March 26, 1925,

(*Communicated by* Prof. S. W. J. Smith, *F.R.S.*)

Abstract.

The simple relation to average current density, previously relied upon to describe low-pressure broadening of the lines in a hydrogen discharge, is shown by examination over a finer range to represent a rough approximation only. Concentration of ions is the obvious controlling factor if the Stark hypothesis be adopted ; recombination of ions on this hypothesis may explain the capacity and inductance curves obtained in these experiments, between 0·3 and 1·0 A.U. This view is further tested by controlling the broadening without altering the current in the tube or the period of the discharge ; for this, a range of widening over which rectified and unrectified discharges show lines differing in width, is provided by a magnetic field. The several effects involved in this experiment are accounted for on the theory that line width depends on the number of charges which surround an emitting particle. A thermionic method is also employed for varying the line width, by drawing into the discharge ions additional to those produced by collision.

I. Introduction.

PREVIOUS researches in the control of broadened spectral lines have either been confined to the variation of gas pressure in the discharge tube, or, when electrical conditions have been studied, they have been confined to the variation of the external circuit : work on this method has been published concerning broadening of Balmer lines over a range of 10 to 50 A.U. The present experiments are an attempt further to disentangle conditions, (*a*) by using a range of 0·3 to 1·0 A.U., in which changes hidden in the wider range might be detected, and (*b*) by using other means of control in addition to that of the external circuit ; this latter becomes necessary in view of a recent suggestion that capacity and inductance control of broadening, at apparently constant pressure, acts by a secondary effect on temperature and pressure.

II. Theory.

The first enumeration of the causes of broadening in spectral lines was given by Rayleigh (Phil. Mag., 29, 274, 1915) and Lorentz (K. Akad. Amst. Proc., 18, 134, 1915). The "impact damping" of Lorentz has since been reinterpreted in terms of the quantum theory by Franck (Anniv. Kais. Wil. Ges., 1921), on the basis of Stark's suggestion (Jahr. Rad., 12, 349, 1915), that the electrical fields between atoms should produce a random disturbance of frequency analogous to the Stark-Losurdo separation. Debye (Phys. Zeits., 20, 160, 1919) and Holtsmark (ditto, 162) calculated that fields between ions should be of the right order of magnitude for such an effect. But the most complete experimental evidence for the Stark explanation of low-pressure broadening is that of Merton and Nicholson (Phil.Trans. Roy. Soc., 216, 1916), who found that the intensity distribution curves of certain lines broadened in condensed discharges agreed with the symmetry and other characteristics found in their Stark separation.

Nevertheless, so far, no satisfactory means has been found of varying the experimental conditions so as to isolate any of the factors controlling the interatomic fields which are assumed. The finding of these factors is to be desired, not only as a further confirmation of the Stark hypothesis, but also as throwing light on the conditions in the discharge tube, and in the stellar atmospheres, where low-pressure broadening appears on a scale beyond reach in the laboratory.

The pioneer attempt at such experimental control was due to Rossi (Astroph. J., September, 1914), who used Milner's theory of the spark discharge (Phil. Mag., 24, 709, 1912), and obtanied with it a linear relation between the breadth of Balmer lines of the order of 20 A.U. and the average current density in the spark. Hulburt (Phys. Rev., July, 1923) accepted Rossi's view of average current density as the controlling variable, and suggested grounds for expecting the well-known narrowing with inductance and broadening with capacity. Miss Hanot, on the other hand (Comptes Rendus, 178, March, 1924) suggested that inductance and capacity act secondarily by altering pressure and temperature relations during discharge.

III. Experimental Detail.

(*a*) *Apparatus Used.*

The hydrogen tubes used were of the usual Plücker type, except in the case of the thermionic tube described in detail below. Various coils, transformers, breaks, were tried in the search for a steady discharge, and a five inch coil worked on 20 volts with a mercury-motor break was finally adopted. For rectification in certain experiments, a large valve of the recessed-electrode type was employed. Gutta-percha covered high-tension inductances were used, and after trial it was found necessary to replace batteries of Leyden jars by two Lodge-Muirhead oil condensers ; the series and parallel combinations of the two halves of each of these provided the variable capacity. The spectrum was analysed by a Hilger constant deviation spectroscope and 20 plate echelon. The magnetic field for the discharge tube involved nothing unusual.

(*b*) *Accuracy of Measurement of Broadening.*

The range of broadening which can be examined by this method is limited by two considerations. Firstly, the region of the spectrum which can be examined in the echelon is never more than twice the order separation, and not much more than 1 A.U. in the case of the present instrument and the line $H\alpha$; secondly, the fine structure of $H\alpha$ covers nearly 0·2 A.U. In the narrow region between these limits, however, the shape of the curve representing the distribution of intensity across the line does not vary greatly. Now the usual definition of " halfwidth " of a line is the distance from its centre at which the intensity has fallen to half its value, so that a measured width depends on the maximum intensity. Two forms have been given (Merton and Nicholson, loc. cit.) of the function which represents this distribution of intensity,

$$I=I_0e^{-kx^2} \quad \text{(i)}$$

$$I=I_0e^{-qx} \quad \text{(ii)}$$

where I_0 is the intensity at the centre, I the intensity at a distance x, and k and q are constants. Equation (i) represents the broadening in a gas at low pressure excited by uncondensed discharges, while equation (ii) represents the broadening of each

component of the line in a condensed discharge. In the previous work, on a range of 10 to 50 A.U., either of these types of distribution has necessitated the microphotometric measurement of the density of image on a spectrogram. Miss Hanot's accuracy, by this means, is of the order of 10 per cent., while Rossi's accuracy in setting a micrometer wire at the point where the intensity of an image is estimated to be half its maximum value, also reached 10 per cent. In the present experiments, the very much smaller range of broadening used allows the intensity curve to remain very steep and approximately constant, and hence the line is always sharply bounded enough to be measured by a visual method with an accuracy of 4 per cent. (or higher in the most favourable experiments). Accordingly the echelon was fitted with a Watson micrometer eyepiece, a white light comparison spectrum being arranged in the lower part of the field of view to facilitate accurate setting of the wire.

(*c*) *Constants of the Echelon.*

If ε be the difference in wavelength corresponding to the separation of successive orders of spectra,

$$\varepsilon=\frac{\lambda^2}{bt},$$

where t is the thickness of the plates, and

$$b=(\mu-1)-\lambda\frac{d\mu}{d\lambda},$$

in which λ is the wavelength and μ the refractive index of the glass for that wavelength.

For $H\alpha$, $\lambda=6563{\cdot}04$ A.U., and, from data supplied by the makers, $\mu=1{\cdot}5711$ and $t=1{\cdot}0467$ cm. The construction of a dispersion curve for this glass then gave $b=0{\cdot}6039$, whence $\varepsilon=0{\cdot}68$ A.U.

The order separation, from line centre to line centre, was then measured with the micrometer eyepiece, when the position of the echelon gave a turning point in the movement of the orders across the field of view—i.e., when the echelon was normal to the beam of light. This was found to be 38·3 micrometer divisions. To the accuracy of the present requirements, then, 56 divisions represent 1 A.U.

IV. Inductance and Capacity Control of Broadening.

In the work of Rossi (loc. cit.) the average current density in the discharge was taken as

$$\frac{\text{charge on condenser}}{\text{half period of oscillation}}\Big/\text{cross section of discharge,}$$

but in the present experiment, with a fixed bore capillary tube, we are concerned only with the average current. If C be the variable capacity, and L the variable inductance, and if we assume the resistance of the tube during discharge is small, the expression above becomes proportional only to

$$\frac{C}{\sqrt{CL}} \quad \text{or} \quad \sqrt{\frac{C}{L}}.$$

Now the experimental results of controlling the width of the line by inductance (Fig. 1) support a linear relation to the average current, until small values of L are

reached—disagreement here may be due to the relative importance at one end of the curve of the inductance in the secondary winding of the coil—but the capacity curves (Fig. 2) do not point to the same relation. These curves each consist of two parts, with a definite discontinuity in direction: experiments which show greater curvature of the lower part show proportionately greater curvature beyond the break, though the latter curvature is always less than the former. Two examples are given in the figure, but the above characteristics occur in all the other series of measurements, made with different types of condenser and discharge. In every case the curvature is opposite to that which would result in a linear dependence of broadening on the average current. This requires explanation, since the period, in

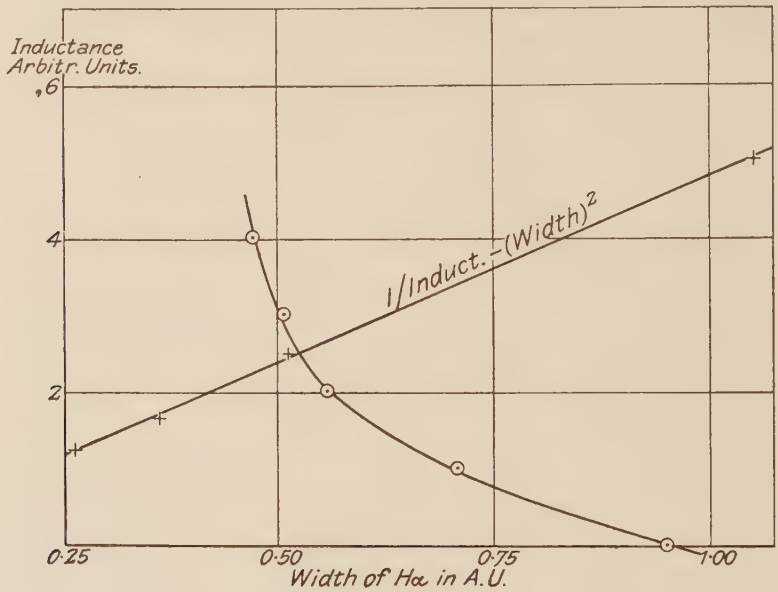

FIG. 1.

the denominator of Rossi's expression, is symmetrically determined by C and L—i.e., so far as period is concerned, capacity and inductance curves should be the same. But the reduction of the expression to $\sqrt{C/L}$ gives a false impression of there being no reason why the regularity of the inductance curve should not also characterise the capacity curve. The following view is suggested as a possible solution of the anomaly; and as leading to a more precise allocation of the responsibility for broadening than to current density.

On the Stark theory, which is subsequent to Rossi's experiments, the number of charged ions should control broadening. The light is emitted by atoms, the electron of each of which is falling back to its two-quantum orbit; while the dispersion of the single frequency related to this energy charge is due to the field maintained by neighbouring charges. The effective field will be larger when the average current passing is larger, but will be a function of recombination as well as of the production of ions. Now, increase of L increases the period without altering the quantity of

electricity discharged at each impulse, and the maximum value reached by the current in each oscillation is decreased. There will be more time for the recombination of ions before the potential next rises to its maximum, and hence a decrease in the field due to the ions which surround the emitting atoms. This will appear as a decrease in line width. Now, increase of C in the denominator of the expression $C/\sqrt{CL}$ acts similarly, but is more than counterbalanced by its increase in the numerator, where it represents a different effect of the capacity, resulting in the creation of more ions than are recombined. Thus we find, on the whole, an increase of the charged neighbours of the radiating atoms. The presence of discontinuous changes of direction in the capacity curves, but not in the inductance curves, is, on this view, a consequence of capacity fulfilling a double function : it can both increase and decrease the number of charged particles, while inductance only decreases their

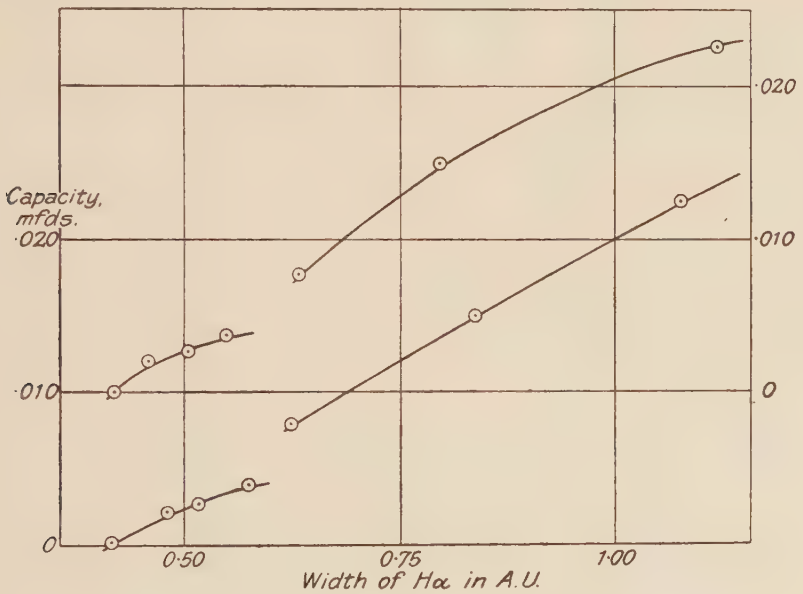

Fig. 2.

number. Now, the time of reorganisation of an excited atom is known from experiments of Wood and of Wien, and has been calculated by Milne ; it is always of the order of 10^{-8} sec. But the time for recombination of a completely ionised atom is a function of a larger number of variables, and though in most cases far greater than 10^{-8} sec., is not determinate. Hence a quantitative relation of the discontinuities in the capacity curve to recombination is not practicable in the present state of knowledge.

V. Magnetic Control.

In the absence of a calculation of recombination of ions, the only other evidence which can be brought in favour of the dependence of broadening on the number of charged ions, instead of simply on average current density, appears to be the following : The concentration of charged ions in the neighbourhood of the radiating

atoms must be varied, while the circuit controlling the current is kept constant. Now, the difference between a rectified and an unrectified discharge carrying the same current should supply this different concentration of ions.

It was found at once that a rectified discharge carrying the same current gave a narrower spectral line than when the main discharge was accompanied by a reverse current of more than half its magnitude. To investigate whether this difference held over a considerable range of widths, condensers could not be used, since their control would destroy the required constancy of period. The effect of a magnetic field was accordingly made use of. [I owe to Dr. Kapitza the suggestion of trying a magnetic control.]

The broadening of the line in a transverse magnetic field was measured for

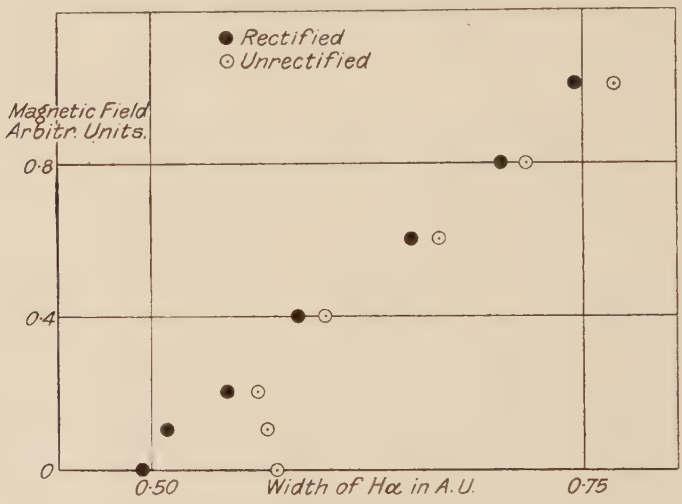

FIG. 3.

rectified and unrectified discharges (Fig. 3). In putting forward a possible explanation of these curves, three facts must be kept in mind :—

(*a*) The broadening is roughly proportional to the magnetic field.

(*b*) The broadening is always less for the rectified than for the unrectified discharge.

(*c*) The divergence between the rectified and unrectified curves is large at first, then decreases, but not to zero.

Consider how far the view we have been taking can explain these characteristics, the view, namely, that width depends on the number of charges which surround the radiating particle. The possible effects of the magnetic field are as follows :—

(i) Zeeman effect.

(ii) A crushing of the discharge against the wall of the tube, according to the deflection of a charged particle at right angles to its flight and to the field. This is known to produce (Kent and Frye : Astroph. J., April, 1913) an increase of the resistance of the tube, hence a decrease of the total current passing ; while the decrease of effective cross section of the discharge increases the current density.

(iii) The several other spectral effects of a magnetic field discussed by Kent and Frye, Waran, and others, e.g., the disintegration of the tube walls, can be neglected in these studies of the single line.

Let us apply the effects (i) and (ii) to the characteristics (*a*), (*b*), (*c*) of Fig. 3.

(*a*) The Zeeman effect, since it is linear with the field strength, will produce a broadening of the kind seen ; before referring this characteristic solely to the Zeeman effect, however, the changes in current density must be carefully examined to see what the maximum disturbance due to effect (ii) could be.

For this purpose the following preliminary experiment was carried out.

To allow for the changes on rectifying, the resistance in the primary circuit of the induction coil had to be decreased slightly. Similar adjustments had to be made to allow for the distortion of the discharge in the magnetic field. These readjustments were in each case made until a milliammeter recorded the same current as was used throughout in the tube circuit. (A milliammeter is of no use in the capacity-inductance experiments, but can be used provided the period is unchanged.) To test whether any changes in breadth of line during the magnetic experiments could possibly be attributed to any of these alterations in the current through the tube, the discharge was varied over a range of 0·5 to 4·5 milliamps., by varying the primary current. The intensity of illumination increases enormously over this range, but the apparent line width only slightly, a result to be expected if the former is controlled by the number of radiating atoms, but the latter by their neighbouring charged particles. Now, the uncompensated milliammeter variations due both to the distortion of the discharge and also to rectification never amounted to more than a small fraction of the range of this preliminary experiment, and cannot therefore be held responsible for the broadening in the magnetic field, which is therefore attributed to the Zeeman effect.

(*b*) Consider next the experimental fact that unrectified broadening is always greater than that in a rectified discharge. On the view we have been taking of the importance of the concentration of ions, this fact appears natural ; the unrectified discharge involves the presence of an additional stream of ions, whose charges will act on the atoms excited by the next impulse in the principal stream. This is the probable reason for the considerable difference between the rectified and unrectified line widths when the magnetic disturbance is zero.

(*c*) The mode of continuation of the curves when the magnetic disturbance is not zero seems, at first sight, strange ; but consideration shows the anomaly may also be explicable on the same view of the charges surrounding the emitting particles.

Since positive and negative ions are moving in opposite directions, the rectified discharge is pressed against one wall of the tube, but in the unrectified discharge there is also another stream of positive and negative ions pressed against the opposite wall. Now, in the very intense fields used by Kent and Frye these two were quite separated into filaments clinging to the front and back walls of the tube. When this condition is reached, the charged particles in the reverse stream would be removed to what is virtually a separate path, and their influence on the emitting atoms of the direct stream would no longer be sufficient to increase widening. Rectified and unrectified discharges would then no longer differ in width. That, even at the strongest fields employed here, this condition is not reached is seen in the fact that

the two curves never coalesce, though they are nearer than at the zero field. Since the fields used are far smaller than those of Kent and Frye, and since careful inspection of the tube never showed the separation of the two streams, the coalescence of the two graphs would not be expected. Some tendency to approach would, however, be expected as soon as the field is switched on, since it is only at zero field that the direct and reverse discharges completely fill the tube and interpenetrate ; only in this condition will the maximum effect of the electric field of the charged particles in the reverse discharge be felt by the radiators, and the maximum difference between rectified and unrectified curves be seen. The wide separation of the curves at zero field, and the decreased separation as the magnetic field increases, are both to be expected from the known effects of a magnetic field, and support the view of the importance of the charges which surround the radiating atoms. Superposed on the Zeeman effect, which is common to both types of discharge, rectification and distortion in a magnetic field seem competent to explain the results seen in Fig. 3.

VI. Thermionic Control.

The concentration of charges around the particles which emit the Balmer lines might also be altered by thermionic means ; electrons, additional to those

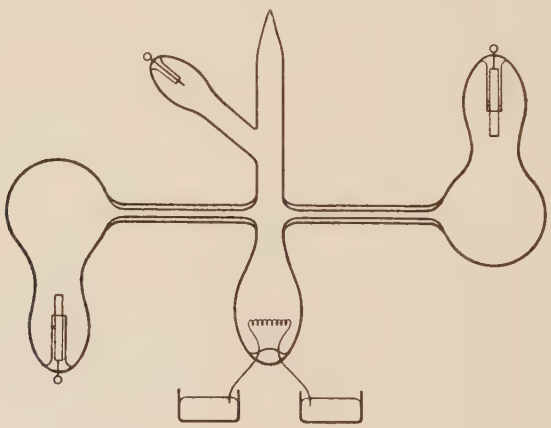

Fig. 4.

produced by the collision mechanism of the tube, might be drawn into the discharge without altering the circuit or the period.

For this purpose a hydrogen tube was constructed with a branch which contained a hot filament. (Fig. 4.)

This tube had to be rebuilt more than once, and a platinum spiral wound round an asbestos fibre coated with lime was finally adopted as a source of thermions ; this was heated by a battery insulated to avoid leakage of the main discharge.

Measurement of broadening was exceedingly difficult with this tube ; in all cases the absorption of light in the echelon makes a very intense source of light necessary, but in this case the current had to be kept low if the number of added electrons was to be large enough in comparison with those already present in the main discharge, to make an appreciable difference to their concentration. The

method is further limited by the occlusion and emission of gas by the filament at different temperatures, " glowing out " by the usual methods being inefficient when an atmosphere of hydrogen has to be retained for spectroscopic purposes.

In spite of these disadvantages, Fig. 5 shows distinctly that the line becomes narrower when the filament is lit up. The decrease in width, $\Delta\lambda$, is greatest for the smallest initial width ; the several initial widths represent the several occasions on which a tube with the same filament and filament current was re-evacuated. The limitation mentioned above, that the original discharge must not produce so many ions that the thermionic source is inappreciable in comparison, is probably the reason for the tendency of $\Delta\lambda$ towards zero at higher initial widths, i.e., at higher pressures. This would account also for the failure to find a positive value of $\Delta\lambda$ even at higher pressures. On the theory we have found reasonable, decrease of line width means fewer free charges present ; the added electrons from the filament,

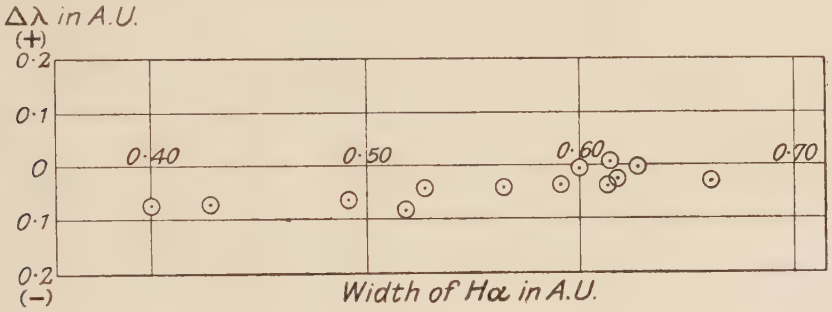

Fig. 5.

on this hypothesis, seem to act by recombination. This is to be expected, since their velocity will be small when they enter the main stream.

I would like to thank Prof. S. W. J. Smith, F.R.S., for the interest he has taken in this work, and for the ready facilities he has provided for carrying it out ; and I am very grateful for the skill and patience of Mr. G. O. Harrison in constructing some of the apparatus required.

Note Added May 8, 1925.

The precise nature of the thermionic effect mentioned in §VI is not of the usual valve type ; it has been pointed out to me by Dr. Kapitza that the insulation of heating battery will prevent any large constant stream of ions of one sign from leaving the filament. The question arises as to the amount of the evaporation of both positive and negative ions together. The differences of potential at the main electrodes will periodically facilitate this, and will draw both into the main discharge ; if recombined in sufficient numbers, this will account for the narrowing seen in Fig. 5. It is hoped that experiments may be devised to throw light on whether these ions would be sufficient for the purpose.

Discussion.

Mr. J. Guild said that this interesting Paper contained some very suggestive results. The author had referred to Rossi's finding that a simple relation existed between the broadening of the lines and the current density, in the rather special sense in which the latter expression was

used. Such a law should give a simple relation between the width of the lines and the intrinsic luminosity of the discharge. Had that point been tested ? Such a result seems unlikely in the case of heavy ions like those of mercury, because in such cases the width can be varied considerably, for a given intrinsic brightness, by varying the design of the tube. What effects would be observed where two or more elements were present in the discharge tube—in the case of a mixture of gases, for instance ? It might be expected, on the author's theory, that the width of a given line would in such cases be affected by the existence of neighbouring charged particles which were not themselves capable of emitting that line. The author had found that the range of his observations was limited by the overlapping of the various orders of the spectrum obtained with an echelon. Could he not, however, measure the broadening from the path difference over which interference would be visible ? The results so obtained would be of lower accuracy, but the range could be extended by this means.

Dr. L. Simons referred to Prof. Wien's work on the "duration of luminosity," or period of phosphorescence of atoms. A luminous atom can be conceived of in classical terms as emitting radiation with an amplitude which is exponentially damped, but the same phenomena can be equally well regarded in terms of the quantum theory as due to the statistical effect of a number of atoms each of which radiates a quantum catastrophically, the radiation being separated from the excitation by a period of time which varies from atom to atom in such a way as to produce a total effect identical with that of exponential damping. The author's results might be regarded from the classical point of view as due to the influence of ions on the decay factor of a damped oscillation, while on the quantum hypothesis the recognised theory of the Stark effect would be correspondingly applicable.

Dr. G. Temple said that it had been found difficult to devise experimental tests for Sommerfeld's prediction of a resolution of $H\alpha$ into a pair of lines, each consisting of a triplet. Shrumm has recently succeeded in verifying this prediction, having photographed the fine structure of $H\alpha$, $H\beta$, and $H\gamma$, but he had to work at the temperature of liquid air. Would it be possible to study separately the widening of each component of such spectral lines ?

Author's reply: With regard to Mr. Guild's suggestion of using limits of interference, M. Procopin is working successfully on those lines for the relation of width to pressure. With regard to the case of elements of higher atomic number, the complexity of their Stark effect would make it more difficult to identify than in the simple symmetrical example of hydrogen. The only relation of width to intensity is that implied in the Merton-Nicholson equations I have quoted. Dr. Simons mentioned Wien's work ; that has certainly given the first clue to the time during which an atom remains excited. When the variation of this is understood, we may get a relation between ionisation and the broadening in a circuit of definite periodicity. Dr. Temple suggested the complication of the relativity structure of a line. For $H\alpha$ this covers at most 0·2 A.U., whereas my narrowest line was about 0·4 A.U. I am now working with a new tube at the effect on the fine structure.

XXII.—ON THE SPECTRA OF THE METALS OF THE ALUMINIUM SUB-GROUP.

By K. Rangadhama Rao, *M.A.*, Madras University Research Scholar.

Received March 16, 1925.

(*Communicated by* Dr. A. L. Narayan, *M.A., D.Sc., F.Inst.P.*)

Abstract.

Continuing the previous work on absorption of light by thallium vapour, the author has now studied the absorption of Tl vapour from λ2400 to λ2000, and that of In from λ6000 to λ2000. The absorption tube was of steel, and provided with quartz windows at the ends, and absorption was studied with a quartz spectograph. Tables were given in each case of the wavelengths of the lines absorbed. The absorption spectra indicate marked similarities. The first members of the series, $1\pi_2$—$m\delta'$, of both Tl and In, are found to exhibit assymmetrical absorption. In both cases there appear at high temperatures and on the short wave side of $1\pi_2$—$2\delta'$ a channelled space spectrum consisting of assymmetrical bands degraded towards the red.

None of the lines of the principal series appeared in absorption, even at the highest temperatures used by the author. One remarkable feature is the very marked absorption of the members of $1\pi_2$—$m\delta'$.

Introduction.

THE study of the spectra of the metals of the aluminium sub-group is of particular interest for, in contrast with the series spectra of the alkali and the alkaline earth metals, $1\pi_2$ instead of 1σ is the highest observed spectral term for the aluminium metals. Further, these elements are trivalent, though the heavier metals of this group, particularly thallium, give stable mono-valent compounds. To account for these spectral and chemical properties, Bohr has recently made the assumption that, of the three outermost electrons in the atoms of these elements, two occupy normally 6_1 orbits, while the remaining one electron is more loosely bound in an orbit of azimuth number 2, and that the arc spectra of these metals give the virtual orbits of this single electron. Measurement of the radiation potentials, as well as a study of the absorption spectra of these metals is, therefore, of special importance, inasmuch as they indicate the orbit of the electron in the normal state of the atom, and test the validity of the above assignment of orbits of the electrons, put forward by Bohr.

Observations of the critical potentials and of the stages in the excitation of the arc spectra have been made on two occasions by Mohler* and others in the case of only one of these elements (thallium), and they find the ionization potential to be 6·08 volts, corresponding to the energy level $1\pi_2$, and lines of the sharp and diffuse

* F. L. Mohler and A. E. Ruark, Opt. Soc. Am. and Rev. Sci. Inst., Vol. 7, p. 819, October (1923).

series corresponding to jumps of the electron into the $1\pi_2$ orbit have been obtained as resonance lines at suitable excitation voltages.

It is well known that the arc spectra of these elements, especially thallium, present easy reversals of the subordinate series lines, which may be due to the fact that the atoms are in an excited state. A certain amount of work on the absorption of thallium vapour has been done during the last few years. In all these investigations the absorption of the vapour was studied only in the near ultra-violet, while in the case of In very little work is done, the only previous work on this being that of Grotrian.

Grotrian* examined the absorption spectra of the vapours of In and Tl up to λ2500 nearly, and found that the lines of the sharp and diffuse series can be reversed, those corresponding to the electron jumps into the $1\pi_2$ orbit, however, appearing at lower temperatures.

Carroll† has also investigated the absorption of Tl vapour, extending his observations up to λ2500.

In a recent Paper‡ on "Absorption and Dispersion of Thallium Vapour" an account has been given of experiments done by the author in collaboration with Prof. Narayan, indicating that the line $1\pi_2$—$1\pi_1$ which, being forbidden by the selection principle, failed to appear in Mohler and Ruark's experiments as a resonance line at the proper excitation potential of 0·9 volt, also remained unabsorbed by a column of non-luminous vapour of the metal. Experiments on dispersion showed that anomalous dispersion was more prominent at λ3775 than at λ5350, which is quite in conformity with the view that $1\pi_2$ is the ground orbit of the electron.

In the present investigation the study of the absorption of the non-luminous vapour of Tl has been extended lower down to λ2000, and the same examination is made in the case of another unique element of this group—namely, In, from λ6000 to λ2000.

Experimental.

The method of experiment was the very simple one of passing light through a steel tube containing the vapour, provided with quartz windows, and examining the emergent light with a quartz spectrograph. This absorption tube of steel was exactly similar to the one used by the author previously, and described in detail elsewhere,§ and, to avoid any possible magnetic effect on absorption, it was heated in a charcoal furnace, through which a powerful blast of compressed air was maintained, the metal being enclosed in a vacuum. The temperature and density of the vapour were gradually raised, and the absorption spectra were photographed at different temperatures. Temperatures of the order of 1,500°C. could be easily obtained by this furnace, though, on account of the softening of the walls of the tube, it was not possible to keep the tube at this temperature for any length of time.

* W. Grotrian, Zeits. f. Phy., Vol. 12, 3 and 4, pp. 218-31 (1922).
† Carroll, Proc. Roy. Soc., A, Vol. 103, pp. 334-339, May (1923).
‡ Narayan and others, Proc. Roy. Soc., A, Vol. 106, pp. 596-601 (1924).
§ Phil. Mag., May (1923).

In many of these experiments the continuous background furnished by a high-frequency spark under water, which passed between two stout aluminium electrodes, was used as the source of light. The distance between the electrodes could be adjusted by a micrometer screw. Fig. 1 shows the electrical connections for this spark. Exposures ranging from 1 to 20 mins. were given, depending on the spectral region to be examined. In the case of both metals, Schumann plates supplied by Adam Hilger, Ltd., were used to photograph the region λ2400-λ2000.

Thallium.

As has been mentioned above, the absorption spectrum of this metal has been previously photographed by the author up to λ2400, so that in the following

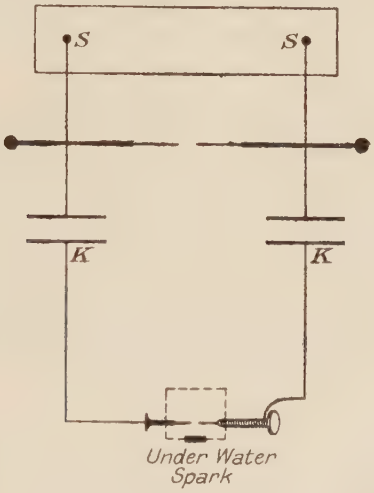

Fig. 1.

table only the additional lines, since photographed in the region λ2400-λ2000, are included:

Wavelength of Line.	Designation.	Remarks.
2315	$1\pi_2$—3σ	
2207	$1\pi_2$—4σ	
2152	$1\pi_2$—5σ	
2119	$1\pi_2$—6σ	
2098	$1\pi_2$—7σ	
2379	$1\pi_2$—$3\delta'$	
2237	$1\pi_2$—$4\delta'$	
2168	$1\pi_2$—$5\delta'$	
2129	$1\pi_2$—$6\delta'$	
2105	$1\pi_2$—$7\delta'$	
2136	.....	These lines do not fit into any series system.
2203	.....	
2532	.....	

The accompanying diagram (Fig. 2) of the scheme of energy levels brings out clearly the orbital transitions involved in the absorption of the above members of the series, and shows that these lines result from the transitions to the lowest energy level, $1\pi_2$.

Plate A is a reproduction of the absorption spectra obtained.

Strip (*a*) is the absorption spectrum from about λ2400—λ2230 A.U.

(*b*) ,, ,, ,, λ2190—λ2090 ,,

*(*c*) ,, ,, ,, λ2400—λ2230 ,,

*(*d*) ,, ,, ,, λ2220—λ2115 ,,

* Portions of the above region taken at higher temperatures.

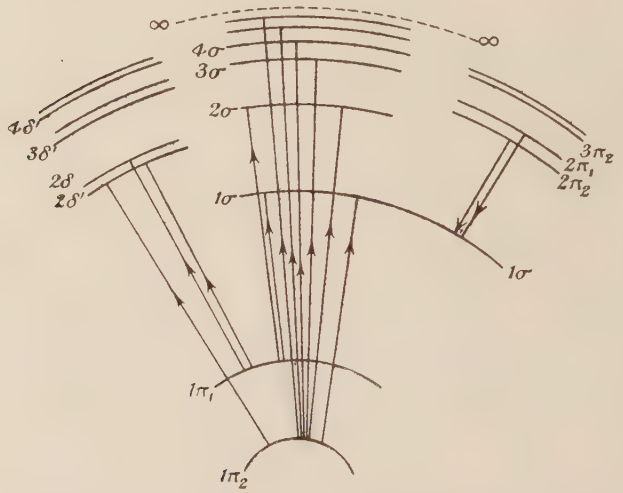

Fig. 2.—Energy Diagram of the Series Systems of Thallium.

From an examination of the above spectra it is easily seen that at each of the lines λλ2379, 2231, etc.—i.e., lines of the diffuse series corresponding to the electron jumps from the $1\pi_2$ orbit—the absorption is very diffuse and complex; almost every line seems to be accompanied by close satellites, which fuse together and merge into the main line, forming a broad band at high temperatures. This feature is most obvious from the lines λλ2379, 2237 [Plate A], which are distinctly seen to be followed by close satellites which, with the increase of vapour density, merge into the main component to form a broad band.

The absorption is much more intense than in the case of the lines of the sharp series.

The assymmetrical development already observed very well in the case of λλ3775 and 2768 is noticed, as is evident from Plate A (*c*), also in the case of λλ2379, 2315.

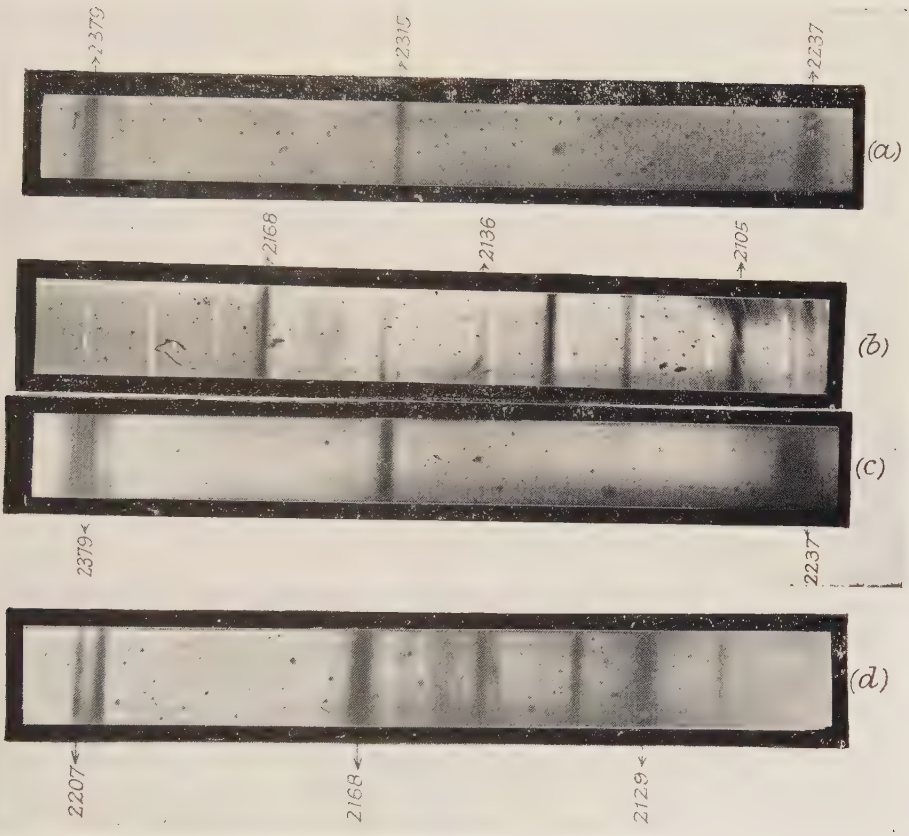

PLATE A.—Ti

To face page 262.]

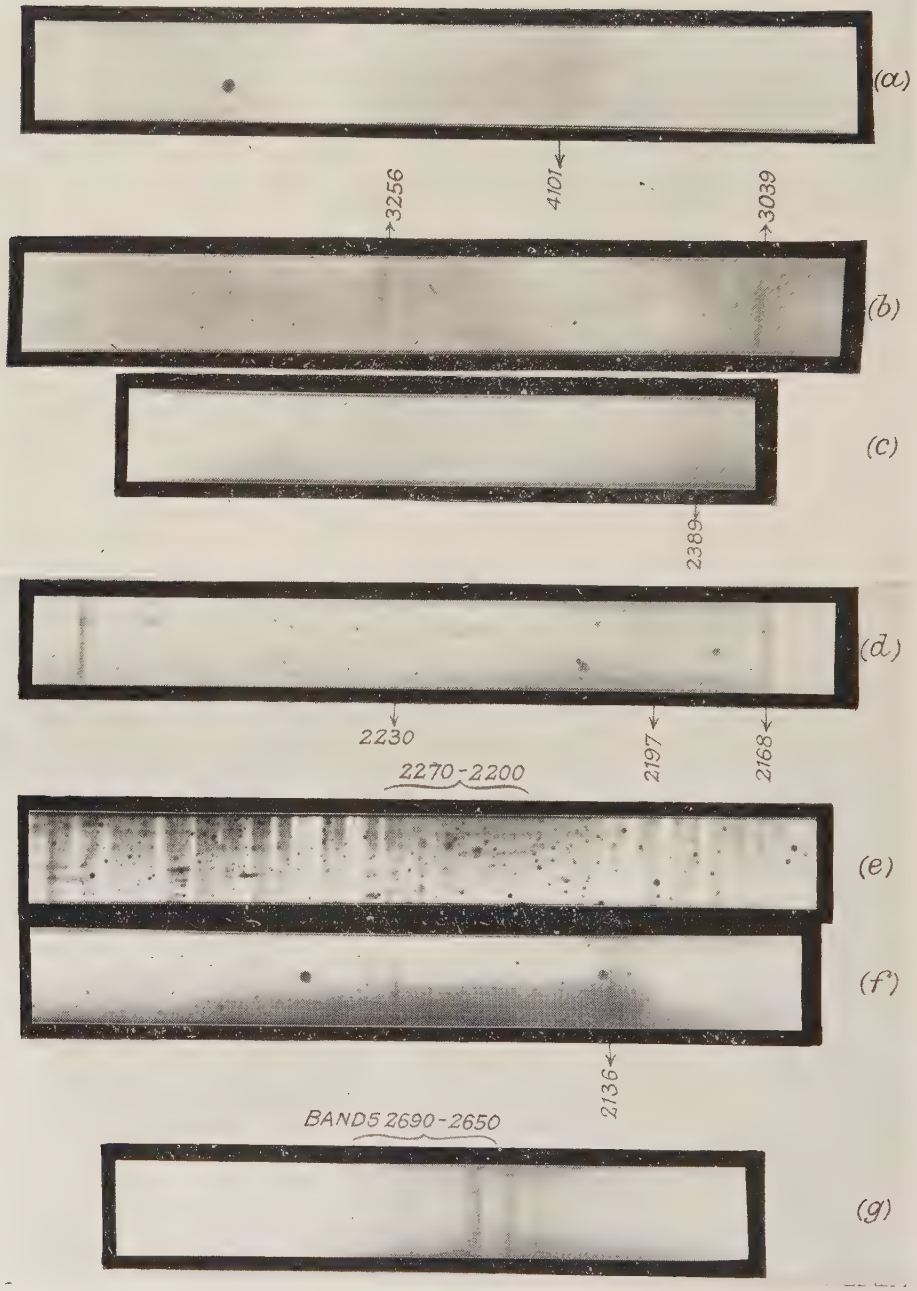

PLATE B.—In.

[To face page 263.

INDIUM.

In the table below is given a list of the absorption lines that have been photographed with Indium vapour, and Fig. 3 represents the scheme of energy levels constructed for indium, just as in the case of thallium.

Wavelength of Line.	Designation.	Remarks.
4501	$1\pi_1$—1σ	
4101	$1\pi_2$—1σ	
2932	$1\pi_1$—2σ	
2753	$1\pi_2$—2σ	
2460	$1\pi_2$—3σ	
3258	$1\pi_1$—$2\delta'$	
56	$1\pi_1$—2δ	
3039	$1\pi_2$—$2\delta'$	
2713	$1\pi_1$—$3\delta'$	
10	$1\pi_1$—3δ	
2560	$1\pi_2$—$3\delta'$	
2522	$1\pi_1$—$4\delta'$	
21	$1\pi_1$—4δ	
2389	$1\pi_2$—$4\delta'$	
2306	$1\pi_2$—$5\delta'$	
2260	$1\pi_2$—$6\delta'$	
2230	$1\pi_2$—$7\delta'$	
2211	$1\pi_2$—$8\delta'$	
2197	$1\pi_2$—$9\delta'$	
2187	$1\pi_2$—$10\delta'$	
2179	$1\pi_2$—$11\delta'$	
2290	.....	These lines do not fit into any series system.
2168	.....	
2136	.....	

Besides these, we have a group of very fine lines at λ2200-2270, as shown in Plate B (*e*).

The chief difficulty experienced in these experiments on the absorption of indium is that, at temperatures as low as about 1,000°C., the vapour exhibits general continuous absorption beyond λ3020 (a fact which does not seem to have been observed by Grotrian), which prevents the photographing of the members of the line series in their developed stage.

The absorption spectra of In and Tl present marked similarities.

As in Tl no trace of absorption lines corresponding to the principal series is detected, but only lines of the sharp and diffuse series were obtained with ease and reproduced in Plate B.

It is of great interest to observe that in the case of both the metals the absorption in $1\pi_1$ series is very feeble, while it is more marked in the lines of $1\pi_2$ series, especially lines of $1\pi_2$—$m\delta'$. This marked absorption in the series $1\pi_2$—$m\delta'$ probably indicates that the transitions of the electron between $1\pi\pi_2$ and δ' orbits is more easy, and consequently more frequent.

The absorption band at λ3039 ($1\pi_2$—$2\delta'$), like the corresponding line λ2768 of Tl, is distinctly assymmetrical, being degraded towards the long wavelength side. In another feature, too, the absorption spectrum of indium proved similar to that of thallium—namely, in exhibiting at high vapour densities and on the short wavelength side of $1\pi_2$—$2\delta'$, a typical banded spectrum which, in both cases, consists of clearly asymmetrical bands shaded off towards the red end. This banded spectrum

(in the case of In) extending over the region 2650-2690 is well brought out in spectrogram *g*, Plate B.

At the same time, it has been found that there is one remarkable difference between the absorption of In and that of Tl, inasmuch as the absorption of Indium is very feeble when compared with that of Tl, though the melting and boiling points of In are distinctly lower than those of thallium. This marked difference between the absorption spectra may possibly be due to the difference in their valencies. From the chemistry of these metals we know that univalent thallium forms a well-defined series of stable salts, while compounds of trivalent thallium are ill-defined and unstable, and those of trivalent In are strong and stable. On the other hand, aluminium is predominantly trivalent. In this and in other ways thallium differs from other members of this sub-group. This strong trivalent nature of In and Al, and the predominantly monovalent nature of Tl, possibly suggests that in the former metals the arc spectrum arises from interorbital transitions of one electron of a group

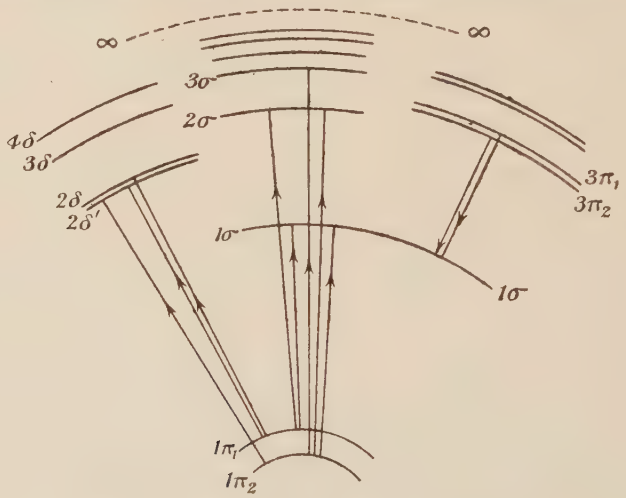

Fig. 3.—Energy Diagram of the Series System of Indium.

of three, while the arc spectrum of thallium arises in the orbitral transitions of the electron having azimuth number two.

However, an account of the great similarity existing between the spectral and chemical properties of the elements of this sub-group, we can tentatively predict the critical potentials of Al, Ga, and In from their known spectral terms, and the following table gives the values of the critical potentials thus calculated for the elements of this sub-group.

Element.	$1\pi_2$ term.	Ionization Potential computed from Quantum Relation.	Excitation Potentials (Volts.)		
			$1\pi_2$—$1\pi_1$	$1\pi_2$—$2\delta'$	$1\pi_2$—1σ
	Cm.$^{-1}$	Volts.			
Al ...	48,281	5·96	0·014	4·002	3·13
Ga ...	48,380	5·97	0·102	4·29	3·06
In ...	46,668	5·76	0·27	4·06	3·01

In conclusion, I desire to express my great indebtedness to Prof. A. L. Narayan for much valuable help during the progress of the work.

DEMONSTRATIONS EMPLOYING THE CATHODE-RAY OSCILLOGRAPH.

Shown at the Meeting on March 27th, 1925.

By Mr. Norman Kipping, of the International Western Electric Company.

I. The Use of the Neon Lamp for Producing a Uniform Time Base.

IT is well known that a neon lamp when shunted by a condenser, the combination being in series with a resistance and battery, passes current intermittently at a definite frequency; the condenser is charged by the current through the resistance until the voltage across it reaches the upper critical voltage of the lamp, whereupon the condenser discharges through the lamp until the lower critical voltage is reached. In the ordinary arrangement the potential drop across the resistance varies exponentially with time, but according to the present system the resistance is replaced by a diode valve which under the conditions of the experiment is run at saturation, so that the charging current to the condenser is constant. The potential drop across the condenser, and consequently that across the diode, then varies linearly with time, and the latter is used for the production of a uniform time base. The frequency is preferably controlled by varying the capacity of the condenser, but alternatively the filament-heating current of the diode may be varied. It is essential that the current through the diode be the saturation current of the latter throughout the charging of the condenser. Wave forms up to a frequency of 50,000 $\sim$ were plotted with this apparatus.

II. An Examination of Some Dynamic Characteristics of Valves.

A valve oscillator with reaction coupling is connected to the oscillograph, so that anode current is plotted against grid voltage, the amplitude of the oscillations being controlled by means of a damping resistance. When two sinusoidal quantities which are in phase are plotted against one another the graph is linear. In practice, however, there is a phase difference between the two quantities mentioned above, owing to the fact that the inductances and capacities employed are not pure, and consequently the oscillograph trace is elliptical in form so long as the straight part of the valve characteristic is adhered to. As the amplitude of the oscillations increases, however, distortion sets in owing to the following causes: (*a*) At the lower values of the grid potential the current approaches zero non-linearly. (*b*) At the higher values of the current, the latter approaches saturation. (*c*) The anode potential varies sinusoidally out of phase with the grid potential, and may even drop to zero for part of the cycle, so that the current in this case becomes zero twice per cycle. In consequence of phase lag the oscillograph trace becomes boot-shaped. Figures varying between the ellipse and the boot were shown, and each of the variables was plotted separately against time. It is found that the maximum obtainable plate current in an oscillating valve is limited not so much by the occurrence of grid current as by the drop in plate potential.

III. Determination of Percentage Modulation and of Distortion in Valve Transmitters.

Percentage modulation is the quantity $\frac{a-b}{a} \times 100$, where a is the maximum and b the minimum amplitude of the carrier wave. This can conveniently be measured by plotting the modulated output current from a valve against the audio-frequency or modulating input voltage. If the modulation is complete (i.e., 100 per cent.) and distortionless the resulting trace will comprise an isosceles triangle whose base is proportional to a and whose height is proportional to the amplitude of the audio-frequency input voltage. If modulation is not complete, the triangle becomes a trapezium of which the longer base is proportional to a and the shorter base to b. Further, there is normally a phase difference between the audio-frequency input and the envelope of the modulated carrier-wave, so that the sloping sides of the trapezium may become ellipses; this does not, however, invalidate the determination of percentage modulation by this method. Over-modulation is shown by the sloping sides of the figure meeting at a point which is not at their ends, and radio-frequency distortion is shown by lack of symmetry in the figure. If the carrier-wave contains harmonics, a series of superposed triangular figures is obtained. In the demonstration the above features were shown at a carrier frequency of about 50,000 $\sim$, and the carrier-wave was also plotted against time both when modulated and when unmodulated, the audio-frequency component of the output being removed by means of a high-pass filter with a cut-off at 3,000 $\sim$. It was shown that when the modulation was 60 per cent. for a sinusoidal audio-frequency wave-form, over modulation at the apex could be produced by adding harmonics to this wave-form.

DEMONSTRATION ON THE DIFFRACTION OF LIGHT BY A SPHERICAL OBSTACLE.

Shown at the Meeting on May 22nd, 1925.

By Prof. A. O. Rankine, O.B.E., D.Sc.

IT was pointed out by Prof. Porter in 1914 that, owing to the existence of the well-known white spot at the centre of a circular shadow, a circular obstacle could be used to project an image of an extended source of light. Each point in the source of light yields its own white spot, and the sum total of the white spots constitutes an inverted image which obeys the same law of magnification as the image due to a pinhole. Owing to the fact that only one point in the source of light can lie on the optical axis a certain amount of aberration occurs with a circular obstacle, but Prof. Rankine avoids this difficulty by using a spherical obstacle, such as a steel bearing-ball. Sources of light of various shapes and about 2 mm. in linear dimensions were made by pasting black strips on a lantern slide ; a ball of about 7 mm. diameter was fixed a few feet away from this, and the image, having a magnification of about 3, was exhibited on a ground glass screen.

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